AD-760 714

OPPORTUNITIES IN HIGH-PRESSURE TECHNOLOGY

NATIONAL MATERIALS ADVISORY BOARD (NAS-NAE)

PREPARED FOR
DEPARTMENT OF DEFENSE

JANUARY 1973

BLANK PAGES
IN THIS
DOCUMENT
WERE NOT
FILMED

OPPORTUNITIES IN

HIGH-PRESSURE TECHNOLOGY

REPORT OF THE

AD HOC COMMITTEE ON HIGH-PRESSURE TECHNOLOGY

NATIONAL MATERIALS ADVISORY BOARD

DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL

Publication NMAB 303

National Academy of Sciences - National Academy of Engineering

2101 Constitution Avenue

Washington, D. C. 20418

January 1973

The quantitative data published in this report are intended
only to illustrate the scope and substance of information
considered in the study and should not be used for any other
purpose, such as in specifications or in design, unless so
stated.

NATIONAL ACADEMY OF SCIENCES - NATIONAL RESEARCH COUNCIL

NATIONAL MATERIALS ADVISORY BOARD

AD HOC COMMITTEE ON HIGH-PRESSURE TECHNOLOGY

Chairman: Professor Harry G. Drickamer
Professor, Chemical Engineering and
Physical Chemistry
Department of Chemistry and Chemical
Engineering
University of Illinois
Urbana, Illinois 61801

Members

Dr. Robert L. Coble
Associate Professor
Department of Metallurgy and
Materials Science
Massachusetts Institute of
Technology
Cambridge, Massachusetts 02138

Dr. Stanley H. Gelles
Materials Processing and
Fabrication Department
Batelle - Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Dr. John B. Goodenough
Lincoln Laboratories
Massachusetts Institute of
Technology
Lexington, Massachusetts 02173

Dr. George A. Samara
Manager, Physics of Solids
Research
Department 5130
Sandia Laboratories
Albuquerque, New Mexico 87115

Dr. Herbert M. Strong
Inorganic and Structures Br.
Physical Chemistry Laboratory
General Electric Research and
Development Center
P. O. Box 8
Schenectady, New York 12301

Professor Clayton A. Swenson
Department of Physics
Iowa State University
Ames, Iowa 50010

Professor David Turnbull
Gordon McKay Professor,
Applied Physics
Division of Engineering and
Applied Physics
Harvard University
Pierce Hall
Cambridge, Massachusetts 02138

iii

AD HOC COMMITTEE ON HIGH-PRESSURE TECHNOLOGY

Liaison Representatives

Department of Defense

Mr. Jerome Persh
Staff Specialist for Materials
   and Structures (Engineering
                    Technology)
Office, Director of Defense
   Research and Engineering
Department of Defense
Washington, D.C. 20301

Department of the Army

Dr. James W. McCauley
U. S. Army Materials and
   Mechanics Research Center
Watertown, Massachusetts 02172

Department of the Air Force

Dr. Dietrich W. Langer,
ARL/LS
Aerospace Research Laboratories
Wright-Patterson Air Force Base
Ohio 45433

Atomic Energy Commission

Dr. Donald Stevens
Assistant Director of Research
   for Metallurgy and Materials
   Programs
Division of Research
Atomic Energy Commission
Washington, D.C. 20545

National Science Foundation

Dr. Robert J. Reynik
Materials Science Division
National Science Foundation
Washington, D. C. 20006

NMAB Staff Officer

Dr. Joseph R. Lane
Staff Metallurgist
National Materials Advisory
   Board
National Research Council
NAS-NAE
2101 Constitution Avenue
Washington, D.C. 20418

iv

ACKNOWLEDGMENTS

Appreciation is expressed to the following individuals who have submitted written material or who contributed to the discussion at committee meetings:

T. H. Geballe

Larry Kaufman

Rustum Roy

W. P. Slichter

Robert J. Zeto

Eugene G. Zukas

These individuals have not reviewed the report and bear no responsibility for its contents.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
National Materials Advisory Board National Academy of Sciences National Academy of Engineering	Unclassified
	2b. GROUP

3. REPORT TITLE

Opportunities in High-Pressure Technology

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report

5. AUTHOR(S) (First name, middle initial, last name)

Ad Hoc Committee on High-Pressure Technology

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
January, 1973	~~232~~ 228	122

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-49-083 OSA-3131	
b. PROJECT NO.	NMAB-303
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	ODDR&E, Department of Defense

13. ABSTRACT

Potential applications of high-pressure technology, with particular reference to Department of Defense needs, were reviewed. The report consists of sections on science, synthesis, sintering and densification, devices, polymers, dynamic high-pressure processes, and high-pressure equipment, all of which evolved from committee discussion. This is followed by 13 appendixes on specific topics.

DD FORM 1473, 1 NOV 65

vi

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Diamond						
Dielectric						
Equation of State						
Ferroelectric						
High Pressure						
Magnetism						
Polymers						
Polymorphism						
Sintering						
Superconductivity						
Synthesis						

Via

CONTENTS

I. INTRODUCTION

In this report those aspects of high-pressure technology likely to have expanding impact on materials research and development, and those aspects of high-pressure research most likely to lead to significant applications in the near future are discussed.

The original charge to the committee was to investigate the opportunities of "ultra-high-pressure technology," with some emphasis on the interests of the Department of Defense (DoD). In the early stages of consultation, certain modifications appeared necessary. It was found impossible to fit potentially fruitful areas into any satisfactory range of pressure clearly defined as "ultra high." The committee, therefore, proceeded to consider high-pressure technology in terms of work distinctly above one kilobar but extending to the highest available pressures. Major emphasis is placed on applications of static high pressure, although shock-wave work is discussed briefly. Contents of this report are largely limited to technology and to research directly applicable to current problems, as was indicated in the committee's charge. However, a brief discussion of the present situation in high-pressure science is included, and several of the appendixes focus on primarily scientific topics.

The report contains a short section on high-pressure science, longer sections on syntheses, sintering and densification, and shorter sections on devices, polymer properties and morphology, dynamic high-pressure processes, and development of high-pressure equipment. Metal forming and extrusion are

not discussed because it was explicitly excluded from the committee's charge; however, it is clear that significant developments in high-pressure technology will occur in this area. Also included are appendices, signed reports by individual members of the committee and by outside experts invited to present material, on specific topics.

The material and conclusions presented in the main body of the report have been reviewed and approved by the entire committee. Much of the material presented in the appendices is used in the main body of the report; however, the appendices have not been reviewed in their entirety by the whole committee and do not necessarily have the endorsement of the committee as a whole. Nevertheless, even though there may be individual differences of opinion about some aspects of the appendices, the latter, as personal reports, represent the opinions of individuals with considerable background and should be useful in planning high-pressure applied research and development.

II HIGH-PRESSURE SCIENCE

The theme of this report is potential high-pressure technology. However, a brief outline of the current situation in basic high-pressure research is not inappropriate in that this research ultimately forms the basis of future technology -- a technology, in most cases, farther in the future than that described in much of this report.

Most of the work done in high-pressure science falls in one of four categories: (1) studies of cohesive energy and the equation of state; (2) studies of structure and morphology, including phase diagrams and synthesis of new phases; (3) studies of atomic and ionic motion in solids (and liquids); and (4) studies of electronic phenomena, including cooperative effects.

While work in the first category has been done for many years, it is still very active. Developments of importance include: the introduction of new techniques (e.g., ultrasonic velocity and x-ray diffraction); extension of the low-temperature, high-pressure range to a few degrees Kelvin at pressures of over 50 kilobars; extension of the static-pressure range plus the refinement of shock measurements; and improvements in theoretical analysis of cohesive energy.

Between 1930 and 1945 Bridgman demonstrated that polymorphic transitions in solids were a common phenomenon. The measurement of equilibrium phase diagrams over an extended range of pressure and temperature has been and is an active field. The development of high-pressure x-ray crystallography has aided in identifying high-pressure phases. The "quenching in" of these phases is widely practiced for both scientific (e.g., geophysical) and practical purposes -- the synthesis

of diamond and cubic boron nitride (BN) being outstanding
examples. Recent work by Phillips and Van Vechten raises
the exciting possibility that one may be able to predict
such transitions, at least for limited classes of materials.
Research areas offering a high potential in terms of both
basic interest and application include metastability, the
rates of first order phase transitions, and the rates of
crystal growth at high pressure.

The study of atomic and ionic motion by tracer
methods has revealed important and useful information concern-
ing the bonding in ionic and metallic crystals and the nature
of impurity sites. The use of nuclear magnetic resonance
(NMR) to study rotational as well as translational motion in
solids, and also in liquids and polymers, is an important
aspect of modern chemistry. The high-pressure applications
have been impressive, and a significant increase in such
applications is to be expected. The study of polymers, in
particular, has important practical applications.

Pressure has been used to study electronic behavior
in solids for about 25 years. Essentially all of the measure-
ments of solid state physics can be carried out in the hydro-
static range to 12 kilobars. During the past 15 years it
has been demonstrated that the quasistatic range to several
hundred kilobars is of great importance. Techniques like
optical absorption and emission, NMR, and Mössbauer resonance
can be applied over an extended range of pressures.

High-pressure studies have been important in the
delineation of the band structure of practical semiconductors
like Si, Ge, and the III-V compounds, in providing an under-

standing of the electronic energy states of a variety of
luminescent materials, and in the study of ferromagne-
tism and anti-ferromagnetism, ferroelectricity, and
superconductivity. High-pressure research has been ex-
tensively used in the study of insulator-metal transitions.
The practical aspects of a number of these studies are
mentioned in other parts of the report.

From the viewpoint of electronic structure, the
basic effect of pressure is to shift one type of orbital
in energy with respect to another. A possible consequence
of this shift is the establishment of a new ground state
for a system, or a ground state greatly modified by con-
figuration interaction. In the past decade it has been
shown that these "electronic transitions" are common
phenomena and that they have chemical as well as physical
consequences. One of the more active branches of high-
pressure science involves the prediction, discovery, and
explanation of electronic transitions. Chemists have been
relatively slow to use high pressure as a variable in
studies of electronic behavior, but the next decade will
probably see a large increase in such work in a chemical
(and biochemical) framework.

Recently, scientific progress has been made in
the understanding of deformation and the effect of defects
on mechanical properties. One can expect considerable pro-
gress in this aspect of high-pressure research in the next
decade.

III. SYNTHESIS

One of the most important applications of high-pressure technology is to the synthesis of new materials. Usually this has involved the establishment of a new crystal structure that possesses advantageous mechanical, electronic, magnetic, optical, etc., properties and can be retained stably or metastably at one atmosphere.

Hydrothermal syntheses typically are done at between 1 and 3 kilobars pressure and are used for a variety of practical materials. Diamond and cubic boron nitride are synthesized in the 50 to 100 kilobar range at elevated temperature. Considerable work is being done in solid-state synthesis in the U.S. and abroad, especially in France, Sweden, Japan, and the U.S.S.R. A great deal of new and exciting chemistry undoubtedly will result from these efforts. There are, however, severe boundary conditions on the syntheses of practically useful materials at very high pressure, the most general of these being that materials synthesized in the 50 to 100 kilobar region at elevated temperature cost several thousand dollars per pound. This limits practical materials to those that can be used in small quantities and offer considerable durability or a high unit value.

A number of the Appendices (including those by Goodenough, Swenson, Samara, Strong, Turnbull, and Drickamer) touch on various aspects of synthesis at high

pressure. Only those materials that may most profitably be synthesized at high pressure and the possibilities, limitations, and problems of each are discussed here. Also listed are some areas of study that could contribute significantly to more efficient and imaginative high-pressure synthesis for a broader range of materials.

"Electronic materials" constitute a class with potentially high value per unit mass. This definition encompasses not only devices for electronic circuits, but also magnetic, luminescent, and ferroelectric materials. Typical materials include hard magnets like CrO_2 and orthoferrites ($LaFeO_3$). One problem with electronic devices is that they usually must be single-crystal material with a minimum of strains and with carefully controlled impurity levels. These conditions can frequently be met in hydrothermal synthesis, and diamonds have been grown with controlled impurities. However, the technique of "quenching in" high-pressure phases has not been conducive to the growth of single crystals, strain-free material, or material of controlled impurity content in the parts-per-million range. An important aspect of further work would be to develop more general methods for growth of single crystals with controlled properties in the higher pressure range. (See Appendix F)

There has so far been very little work done on developing high-pressure luminescent or photochromic materials. These applications could involve small amounts

of high-unit-value materials. High-pressure phases of
phosphors could involve higher luminescent efficiencies
and different lifetimes, as well as more stable photo-
chromic states, than the corresponding low-pressure phases.
In this regard, more crystalline polymers, especially in-
organic polymers, offer the possibility of luminescent
material of stability over a large range of temperature.

High-pressure experiments have been important in
understanding the phenomenon of superconductivity, and a
number of high-pressure phases have proved to be super-
conducting where the low-pressure phases are not. Since, in
a number of cases, superconductivity is associated
with metastability, the possibility of quenching in high-
temperature superconductors is intriguing. The econ-
omic potential of electrical transport by high-temperature
superconductors is enormous. Much of the discussion has
centered around the possibilities of the metallic phase
of hydrogen, but it is difficult to give any prognosis
which is more than a guess. According to various cal-
culations, hydrogen will become metallic at a pressure
which is variously estimated between 0.8 and 6 megabars--
most calculations give a range of 1.5 to 3.0 megabars.
A number of analyses indicate that the high-pressure
phase would be a high-temperature superconductor
(T_c 60-200 °C), although this conclusion is by no means
universally accepted. Grave doubts arise concerning
the probability of retaining the high-pressure phase meta-
stably. (See Appendix F) It would appear that even if

bulk metastability were a possibility, the material would decompose by surface instability. With the present state of knowledge it is difficult to offer even tentative conclusions, and a number of investigations would be helpful. One diatomic molecular crystal, iodine, has been shown to be metallic above the 130 to 170 kilobar range. An investigation of its superconducting properties would be very helpful. Also, aromatic hydrocarbons like pentacene and hexacene become metals or semi-metals above 200 kilobars. Investigation of the metallic transitions (and ultimately the superconducting properties) of solid Br_2, Cl_2, F_2, and hydrogen-containing materials such as methane (CH_4) and ammonia (NH_3) would advance both the art and the understanding of high-temperature superconductivity. It is known that at moderate hydrogen pressures materials like palladium take up atomic hydrogen in a ratio of several atoms of hydrogen per palladium atom. It would be of interest to know the superconducting properties of these materials at sufficiently high pressure and hydrogen concentration.

The synthesis of diamond, and later of cubic boron nitride, has been a tremendous incentive to high-pressure work. Currently, much research is devoted to making diamond (or BN) with particular characteristics or to making it more cheaply. There have been, of course, strong incentives for making a harder material, but the possibilities (discussed in Appendix D) for such a material seem slight.

It is, however, possible that high-pressure phases which
are not as strong as diamond may have either chemical or
high-temperature properties of technological significance.
It has not so far been possible to form solid solutions of
diamond with BN, SiC, or other hard materials. At suffi-
ciently high temperature and pressure it might be done, and
the resulting materials could be of considerable interest.
Strong discusses in some detail (Appendix D) the variety
of new phases of inorganic solids that have been observed.
The sintering of diamond and other materials is discussed
elsewhere in the report.

A relatively uninvestigated field is that of
using very high pressure to produce new catalysts. These
materials satisfy the requirements of high value per unit
mass and repetitive usage. It is clear that the form and
structure of a material, as well as the chemical composition,
is important in its catalytic activity; e.g., it has recently
been demonstrated that 10 to 20 angstrom metallic alloy
particles have very different catalytic (and electronic)
properties than do larger particles. It would appear that
high-pressure phases of many materials such as oxides
could have different, and possibly better, catalytic
properties than their low-pressure counterparts. It may be
possible to produce materials with unusual oxidation states
at high pressure, and these may have considerable potential
as catalysts. Involving different stoichiometries and
different degrees of doping in the high-pressure products

might also be feasible. People working in catalysis are generally unfamiliar with solid-state chemistry at high pressure, and vice versa. It would be desirable to encourage interaction.

The usual high-pressure polymerization from the gas phase or in solution occurs in a pressure range generally below that considered here. While the possibility of formation of polymers in the solid state at relative high pressure exists, the expense involved would eliminate these materials for most practical applications. However, as mentioned earlier, it may be possible to prepare polymers for special electronic or luminescent applications. In this regard, the field of inorganic polymerization appears to have special relevance.

Traditionally, solid-state synthesis at high pressure generally has meant the preparation at high pressure of a new crystal structure that can be retained metastably at one atmosphere. In general there are changes in chemical bonding, but the electronic effects usually have been subordinated to the structural effects. As discussed by Drickamer (Appendix M), pressure has a profound effect on electronic energy levels. Under many circumstances the relative shift in energy levels with pressure is sufficient to give a new ground state, or a ground state greatly modified by configuration interaction. It has recently been demonstrated that these new ground states may have very

different chemical as well as physical properties. The
chemistry of these new ground states has been very little
explored to date. It has, however, been shown that for many
systems it is possible to estimate the possibility of a
thermal electron transfer (an electronic transition) from
the change of location and shape of appropriate optical
absorption peaks. This area deserves further exploration
and systemization for its potential practical applications.

Thus far in this report the synthesis of materials
at high pressure for practical applications has been em-
phasized. There is, however, another aspect of high-
pressure solid-state chemistry which has considerable
practical potential: this lies in the area of the analogy
between the effects of pressure and of composition changes
on physical and electronic properties.

An interesting example of potentials in this
area lies in the studies of metal-insulator transitions in
solid solutions of Cr_2O_3-V_2O_3 conducted by McWhan and his
colleagues at Bell Laboratories. They have demonstrated
that changing the amount of Cr_2O_3 in the material is in
many ways analogous to changing the pressure insofar as
electronic properties are concerned. A second example
involves studies of prototypes of hemoglobin such as hemin
and hematin which demonstrated that the effects of pressure
are in many ways closely analogous to the effects of adding
electrophillic groups to the periphery of the molecule.

The study by Goodenough and his co-workers of the high-spin to low-spin transition in the MnAs-MnP system, where 1 kbar pressure was shown to be equivalent to 1 percent P is another striking example. However, there may also be important differences between pressure and composition effects, as has been emphasized by Goodenough and demonstrated by Kafalas, et al for the system $Ca_xSr_{1-x}MnO_3$. For many systems, properties which could be practically advantageous but which cannot be quenched in may be observed at high pressure. If the analogy between pressure effects and composition effects for the type of system involved is clearly understood, it may be possible to prepare a material with the relevant properties at lower pressure, or even at one atmosphere.

The practical use of high-pressure synthesis would be greatly increased by more thorough understanding of a number of problems. These include the causes and control of metastability, the rates of first-order phase transitions, the rate of crystal growth, the probable pressure range of first-order phase transitions in various categories of materials, the probable pressure associated with electronic transitions of various types, and the relationships between various types of chemical doping and of pressure on various properties. In many of the above cases a significant start has been made on the solutions. An improvement in our predictive power could greatly reduce the time and expense involved in searching for practical materials.

IV. SINTERING AND DENSIFICATION

High pressure sintering and densification is an important aspect of high pressure technology, and one which will probably increase in significance in the immediate future. (Appendices A, B and D deal with various aspects of sintering.) Densification to theoretical or near theoretical density depends in part on the ability of particles to deform plastically by glide or creep to give more intimate contact between adjacent particles. The relevant operating variables are temperature, pressure, and time, with the first the most important and the last probably the least significant. The degree of success depends also on internal variables such as particle size and size distribution, purity of material, the initial stress condition of the particles, their surface condition (presence of surface impurities or absorbed gases), and the possible use of sintering aids or binders.

Most sintering to date has taken place at one atmosphere or under modest pressures,up to 1 to 2 kilobars. (See, however, the discussion of diamond below.)

Pressure may act to add to the interfacial energy as a driving force for densification and tend to induce plastic flow as a mechanism for densification. For relatively low pressures with specific materials in which diffusion provides the mechanism of densification it is probable that the diffusivities will be decreased by the applied pressure. However, this effect appears to be econdary.

The advantages of using pressure include:

1. The possibility of using lower temperature and thus preserving a finer grain sized microstructure,

e.g., preventing grain growth which is
accelerated by temperature.

2. The ability to produce higher density mater-
ials with less binder.

3. The possibility of staying within the stability
range of a high-pressure phase while sintering
--e.g., diamond vs. graphite.

4. The possibility of achieving densification in
single-phase covalent-bonded materials which
do not undergo densification under pressureless
sintering. Fine-grained high-density hot
pressed shapes of SiC, Si_3N_4, and B_4C are
commercially available.

There are, however, definite limitations to the
use of pressure in the sintering process. Besides the
expense of high-pressure equipment, there are limitations
on the size and shape of pieces which can be sintered,
especially at the higher pressures, as well as problems
in pressure uniformity. High-pressure sintering is a
batch process and is therefore more expensive than
processes which can be operated continuously. Frequently
the economics involve a trade-off between temperature
and pressure.

We mention below a few of the types of material
for which high-pressure sintering and compaction have
proven to be practical.

Most metal powders can be consolidated at 1
to 5 kilobars pressure at temperatures less than $0.5T_m$.
An example of this pressure-temperature trade-off is
beryllium powder which may be consolidated at 900° C
and 10,000 psi or 1100° C and 2000 psi. High pressure

is especially advantageous for very high melting materials which at the highest available temperatures still have considerable resistance to flow.

A second practical application involves dielectric materials where pressure consolidation can give materials with low dielectric loss, high dielectric strength, high dielectric constant, non-linear response, a stronger piezoelectric response, etc.

Fully dense optical quality ceramics have been made from a wide variety of substances. Such materials are used as optical windows, radiation detectors, laser hosts, and electro-optic devices. Materials which are sintered below 1 kilobar include MgO, Y_2O_3, Al_2O_3, $MgAl_2O_4$, and the family of ferroelectrics consisting of lanthanum-doped lead zirconate-titanate. These materials were all first made by pressure sintering and still are being made by this process, although pressureless processes have also been developed for all except Y_2O_3. Y_2O_3 is an excellent host for rare earth ions and is transparent from 0.3 to 8 microns. Single crystals can only be grown in small sizes not suitable for applications. The sintered material can be made fully dense with transmission characteristics which closely resemble the single crystal in sizes up to approximately 1 inch in diameter.

It is possible to sinter electronic materials
to give better mechanical properties as well as improved
electrical and thermal properties which result in longer
lifetimes. A recent development is the sintering of doped
silicon-germanium alloys for thermoelectric applications.
It is of interest that, for this material, a moderate in-
crease in sintering pressure from 28,000 to 32,000 psi
gives marked improvement in alloy homogeneity, mechanical
strength, and electrical and thermal properties. It seems
probable that there will be a variety of other thermoelectrics
and semiconductors produced by similar processes.

Structure sensitive magnetic properties such as
initial permeability, B-H characteristics, and lossiness
are affected by grain size, grain boundaries, and inhomo-
genieties. Thus, pressure sintering offers a possible
method of controlling density and texture, and therefore
the magnetic properties of polycrystalline materials.
The method has been applied commercially for ferrites
($MeO \cdot Fe_2O_3$) and garnets ($3Me_2O_3 \cdot 5Fe_2O_3$). The fact that
pressure sintering can reduce the required temperature is
an important advantage here, as it is frequently necessary
to control closely the valence state of the transition
metal ions in ferrites and garnets, and this can best be
done at lower temperatures.

The most significant development in sintering of
useful materials in the higher pressure range (50 to 100
kilobars) is that of diamond (and possibly also cubic BN).
There have been a number of reports of successful sintering

both in the U.S. and Russia. The details are only poorly
known at present, but it apparently usually involves a
binder in significant quantities. (Strong, in his chapter
in the Appendix, discusses a sintered diamond-tungsten
carbide product which appears very useful for machining.)
H. T. Hall at Brigham Young University has prepared sintered
diamond with a variety of binders. Some of these products
have undergone fairly extensive tests in potentially prac-
tical service. Sintered diamond could have a wide variety
of applications in machining, rock cutting, wire drawing,
etc. There have been a number of reports that Vereschagin's
group in the U.S.S.R. have developed sintered diamond cutting
tools with impressive characteristics. The requirements for
commercial application in competition with single-crystal
diamond are rather severe in terms of friability, cutting
ability, durability, etc. It would appear probable that
techniques can be perfected to make sintered diamond com-
petitive for many, if not all, such applications.

A possible application of interest is the manu-
facture of pistons and vessels for high-pressure work to
extend the pressure range. This problem is discussed
briefly in a later section.

Many of the problems encountered with diamond
are also present with refractory materials and solutions
of the diamond problem will be applicable in a high degree
to oxides, carbides, borides, and nitrides.

It seems very probable that high-pressure compaction methods will be applicable in the growing field of composites which are finding an increasing variety of applications.

A process related to compaction and sintering is high-pressure bonding in metal-metal, metal-ceramic, and ceramic-ceramic systems. A good example is the bonding of fine-grain alumina discs to each other and to metals. The isostatic process has great potential in this operation.

The application of shock techniques to these processes is discussed briefly in a later section.

There are a number of aspects of sintering and densification where a better understanding of the variables would increase the practical possibilities. These include: the effect of surface morphology and surface cleanliness on bonding; the function of the bonding and/or binder (indeed different binders may have quite different functions), and a more quantitative understanding of the tradeoff between temperature, pressure, and time for various categories of materials.

V. DEVICES

In a previous section we discussed the high-
pressure synthesis of materials that could be recovered
for application at one atmosphere. Here we discuss
materials with properties directly useful at high pressure.
Perhaps the most obvious application is the pressure gauge.
Techniques are well known for measuring static pressure
at equilibrium. The usual standards are the resistance
of manganin for hydrostatic pressures to 30 kilobars and
electrical resistance discontinuities or maxima or changes
in lattice parameter for higher pressures. While these
techniques are not completely satisfactory we shall not
concern ourselves with them here.

It is, in principle, possible to make use of
phase transitions (e.g., insulator-metal transitions) or
changes in energy of optical absorption or emission peaks
to measure impact pressures on rapidly oscillating
pressures. Optical transitions have the advantage of high
speed (10^{-10}- 10^{-12} seconds) and require only small
samples. The technological problems involved in develop-
ment of truly practical devices are severe.

In several places in this report it has been
mentioned that a general effect of pressure is to shift the
energy of one type of electronic orbital with respect to
another. This relative shift could have a number of applica-
tions besides pressure detection. One such possibility is
the pressure tuning of lasers. A second application is the

change of the absorption edge of photocell detectors to shift the region of maximum sensitivity to lower or higher energy. The application of uniaxial stress might also be useful in these applications.

A different high-pressure application would involve the absorption of shock or impact. The obvious mechanism would be to make use of the latent heat and/or volume change at a first order transition. One would like transitions which occur at modest pressures if the idea is to protect a material from high-pressure shock. The rubidium halides have transitions near 4 or 5 kilobars with large volume changes, but small latent heats. They have low mechanical strength. Melting or vaporization at high pressure would supply large latent heat. The actual development of a practical device would require a detailed knowledge of the particular application.

VI. POLYMER PROPERTIES AND MORPHOLOGY

Moderate pressures have been widely used to
synthesize polymers in the gaseous and liquid phases.
We make no attempt to review this area in the report.
Solid-state polymerizations at high pressure have been re-
ported but they are without apparent direct application at
this time. Pressure has, however, an important potential
role in understanding better the structure and properties
of commercially useful polymers. The situation is reviewed
in the Appendix by W. P. Slichter. We summarize his comments
briefly here. There are three categories of structural or-
ganization for bulk polymers: (1) crystalline regions; (2)
rubbery structures, and (3) glassy arrays. The relative
stability of these different arrays depends on the molecular
structure, on the temperature, and on pressure. There are
two temperatures which characterize the material, T_m, the
melting temperature, and T_g, the glass point, which possibly
is related to the point at which the free volume disappears.
Measurements of the effect of pressure on T_g have been made.
It would be most useful if these could be related to other
pressure sensitive parameters such as heat capacity, thermal
expansion coefficient, and molar volume.

Partially crystalline polymers have a morphology
that is pressure dependent. Crystallization at pressures
in the order of 10 kilobars leads to morphologies in which

the crystalline lamellae are 10^3 Å thick or more and consist
of chains in extended conformations. Crystallization at one
atmosphere leads to lamellae of folded chains with a fold
length of ~ 100 Å. The work to date has been largely on
polyethylene; it is not entirely clear whether the modified
forms have properties which would be commercially attractive.

An important aspect of high-pressure studies of
polymers involves following the motion of molecular sub-
groups in all three regimes by nuclear magnetic resonance
relaxation. Relative to the study of ordinary crystalline
materials, high pressure studies on polymers are sparse,
but they have yielded enough information to indicate that
they should be pursued with some vigor.

The use of polymers in composites and the develop-
ment of polymers capable of high-temperature, high-pressure
applications (including inorganic polymers) make this an
area of great potential importance.

VII.   DYNAMIC HIGH-PRESSURE PROCESSES

In this report we have confined ourselves
largely to static high-pressure processes for a number
of reasons. However, it seems advisable to outline the
potential impact of dynamic processes on technology. These
matters are touched upon in a report by Samara in the
Appendix, and also in the discussion of Gelles.

Shock measurements have long been important in
high-pressure science in establishing equations of state
over a very large range of compression and in locating phase
transitions. Recent advances in shock-wave science in the
understanding of dynamic yielding and elastic- plastic
phenomena, in material strength and fracture, and in
measuring the electrical and magnetic response in solids
like quartz, germanium, and iron alloys have extended the
usefulness of shock studies. These new developments are in
their early stages and with proper support should add con-
siderably to the possible usefulness of the technique.

There at present are a number of areas where
dynamic techniques are commercially feasible or clearly
potentially so. These include:

1.   Explosives bonding
2.   Explosives forming,
3.   Shockwave hardening,
4.   Dynamic synthesis.

The first three techniques are primarily applied to metals and, although metal forming was specifically excluded from the committee's charge, a few sentences on these techniques would not be inappropriate. (See Appendix C for a more extensive discussion.)

Successful explosive welding and cladding has been performed on a number of combinations like bismuth-steel, aluminum-titanium, aluminum steel, and copper-molybdenum, where there are large differences in melting point so that conventional methods are unsuccessful. This can occur since melting is not necessary, and is in fact undesirable because of grain growth. Clean surfaces are essential. Explosive cladding is now used for material for coins. It holds promise for wear, erosion, and corrosion resistant applications and possibly for metal composites. Plates up to 300 ft^2 and cylindrical shapes of various sizes have been explosively clad. Explosive welding also has been used in joining dissimilar metals for marine applications and for welding tubes to plates in heat exchangers and boilers.

In the above processes, pressures of tens to hundreds of kilobars are required. In explosive forming, on the other hand, pressures of several kilobars are ample. The possible advantages of the technique include: meeting close tolerances on objects of all sizes; forming unsymmetrical and unusual shapes; forming large work pieces; utilizing cheap materials; utilizing a short response time; and forming metals difficult to form by conventional means.

Shock-wave hardening has been employed in the surface hardening of rails and crusher jaws. Pressures ranging from 10 to 100 kbars are used, and the hardness decreases with increasing depth. Both stress amplitude and duration of the shock wave affect the hardening -- a longer pulse of lower amplitude can be as effective as a short high-amplitude pulse. Recent studies on Hadfield steel over the range to 500 kbars indicate that it is the dislocation density and not the specific microstructure which controls the hardness of the steel. It is not yet clear whether this conclusion is general. An increase of hardness by a factor of four in 200 kbars has been observed. The field is not well developed, but holds considerable promise.

The field of shock synthesis is relatively new and comparatively unexplored. A number of groups have synthesized diamond by this technique. Du Pont has demonstrated the capability of applying high shock pressure to a relatively large volume with good product recovery. Information is not available to the committee on the properties of the recovered diamond or its usefulness on various applications. The economics compared with other processes are not known to this committee. It would appear that the technique would apply primarily to materials of high unit value.

Explosive compaction and sintering have received relatively little attention to date. It has attractive possibilities where very high pressure and temperature are involved. These variables can be controlled somwhat independently by changing the packing of the initial charge. There may be problems with stored strain and cracking of the resultant product. It is an area which deserves considerable further investigation.

A final application related to shock work involves the use of high-power lasers to generate an implosion. Investigations of this possibility are under way in several laboratories.

VIII. <u>DEVELOPMENT OF HIGH-PRESSURE EQUIPMENT</u>

A problem of at least potentially practical interest is the development of equipment to permit research at higher pressures. There is no agreement within the committee concerning the pressure limitations on existing equipment of various types. (See Appendix D for one set of opinions.) While there is a divergence of opinion, it appears that among techniques which have been in use for some time, it is certainly not possible to make any static measurements even on the smallest samples at pressures approaching the megabar region. For shock-wave work pressures of several megabars are not uncommon and 30 megabars has been reported in Russia. However, the temperatures in these experiments are too high and the times too short to permit many important experiments. Also, such pressures are obtained in only very stiff materials.

A significant extension of the pressure range could certainly yield important new scientific information and could influence technology, although the unit expense of the product would probably be very high. A number of laboratories are involved in efforts to extend the static pressure range. Two which have aroused considerable general interest are briefly mentioned here.

N. Kawai in Osaka, Japan, has developed and worked extensively with the "collapsing sphere" technique

first proposed by von Platen. He estimates that pressures of several megabars have been obtained. The data published in his papers do not permit an accurate evaluation of his estimates. The technique could, in principle, yield very high pressures if the problems of carbide deformation under these conditions are overcome. Further tests and much more detailed data would be of considerable interest.

At the Institute for High Pressure Physics of the Academy of Sciences of Moscow, under the leadership of L. Vereschagin, development of a device in which it is hoped to reach 2 megabars or higher has been underway for at least seven or eight years. The features of this development, as far as can be ascertained, include multiple staging, the employment of sintered diamond pistons and cylinders, and the use of a 50,000-ton press which has been the subject of considerable discussion.

The use of sintered diamond for high-pressure equipment has much to offer and has been discussed in various phases for a decade or more. There is no reason why it could not be tested in simpler smaller scale devices like the supported taper cell. Multiple staging or equivalent internal support in some form will almost certainly be essential in any extension of the pressure range. It would appear, however, that most forms of multiple staging as well as the use of new materials like sintered diamond could be tested in at least the initial stages without extraordinarily large presses.

Since one of the most important reasons, if
not the prime objective, of the extension of the pressure
range is to obtain metallic hydrogen and to test its
properties, including superconductivity, operation at
relatively low temperatures will be required. Thus, it
would seem very desirable to keep the apparatus reasonably
small in scale.

A development of particular interest is the
high-pressure apparatus developed by R. S. Hawke and
his colleagues at Livermore. Using magnetic flux com-
pression, they have obtained pressures of one to several
megabar in compressible materials like lucite. The
compression is isentropic so that the temperatures, while
elevated, are very much lower than those encountered in
shock experiments at comparable compressions. The appar-
atus has very interesting possibilities. In particular,
it may be possible, using this device, to establish rela-
tively quickly, at least the dimensions and boundary
conditions on the problem of making metallic hydrogen.

It would be useful to have materials such as
sintered diamond and various support and multiple-staging
devices tested in this country, preferably at a place
(or at places) with appropriate experience in development.
It would be important that the information be immediately
accessible to the high-pressure community. In the opinion
of the committee, pending further analysis, it is not clear
that, at this stage, an effort built around a very large
press is required.

IX. CLOSING REMARKS

Each section of the report contains suggestions and prognosis for future work, as do many of the individual reports in the Appendix. It would therefore be redundant and difficult to repeat recommendations about specific substances, techniques, or applications.

It may be worth emphasizing one general aspect, however. Both high-pressure technology and many aspects of high-pressure research have been very empirical to date-- more so perhaps than many other fields. Not only have new phenomena been uncovered largely by serendipidy, but it has not generally been possible to predict from one example (or a few examples) of a new phenomenon under what conditions and for which substances one might observe related results.

There are distinct signs that in a number of areas (e.g., first-order phase transitions, electronic transitions, metastability) some rudimentary predictive capacity is developing. One can reasonably hope that similar developments in areas like sintering, rates of phase transitions, etc., will soon appear. The development of predictive capacity centers on the availability of a sufficient amount of the <u>right</u> <u>kind</u> of <u>selective</u> data plus some imaginative and broad-gauge analysis. The development of this predictive capacity constitutes a very "high leverage" situation in terms of introducing new applications. The strong support of interaction between experimentalists with a sound understanding of principles and theorists or analytical engineers with broad interests is a very wise and economical investment.

APPENDIXES

The following reports have been written by individual committee members and consultants. While they have not been reviewed by the committee as a whole, they contain information and opinions by experts in various aspects of high-pressure research and developments.

APPENDIX A

HIGH-PRESSURE SINTERING

by G. A. Samara
Sandia Laboratories, Albuquerque, New Mexico

1. INTRODUCTION

One area of high-pressure work that is becoming
an important fabrication process for consolidated poly-
crystalline materials and ceramics and that is bound to
be of added future importance in materials technology
is high-pressure sintering or hot pressing. This process
has been limited almost exclusively to rather low pressures
(< 1-2 kbar), and the higher pressure potential remains
largely unexplored. Although the pressure range currently
used is so low as to be outside the present committee's
charter, this area has been and undoubtedly will continue
to be one of the most promising for the utilization of
pressure in materials technology. In particular, pressure
sintering techniques hold promise for solving some of
DOD's pacing materials problems. Thus, it is worthwhile
to comment briefly on this area. A description of early
work and the current state-of-the-art can be found in the
first two references cited.

Pressure sintering is not a cure for all material
compaction and densification problems. Rather, while the
process has both adaantages and severe limitations, it is
occasionally the only means available for producing cer-
tain properties and, in this situation, is most useful
and advantageous. Among the strong advantages of pressure

sintering are its ability to: a. produce uniform high density (up to theoretical) materials, and b. control the microstructure (grain and pore size), thereby yielding high-strength materials often with improved mechanical and physical properties. Control of microstructure is achieved through the lowering of the sintering temperature and time at temperature over that needed in the conventional (pressureless) sintering process. The lower temperatures and times needed make it possible to sinter materials that cannot be sintered by conventional means (e.g., materials with high vapor pressures and low melting points and those that decompose at normal sintering temperatures).

The present limitations of the process are those imposed by apparatus and relate to the size and shape of sintered bodies that can be produced and to the pressure range that can be covered. The process also is largely a batch operation and, therefore, relatively costly. The added cost has to be justified by the nature of the application since pressure sintering is not merely a substitute for conventional methods. In fact, the use of pressure (other than in research efforts) will generally be avoided if desired properties can be achieved by other means such as the use of sintering aids when such aids can be tolerated.

2. THE PROCESS

Pressure sintering is commonly accomplished through the application of uniaxial pressure using a piston and cylinder (die) apparatus. The sample

(powder or powder compact) is sometimes encapsulated in a
refractory material to prevent sample contamination.
Heating is by electrical resistance or electrical induction
means. The sintering can be done under vacuum or in a
neutral or reactive (e.g., reducing or oxidizing) atmosphere.
Graphite is the refractory material most commonly used at
low pressures (< 1 kbar). Oxides such as ZrO_2 and carbides
such as SiC have also been used at these and higher pressures.
Metals such as TZM, a titanium-zirconium-molybdenum alloy,
are also commonly used in vacuum pressure sintering.
Pressures have been largely limited to less than 2 kbar,
and temperatures as high as 2000 - 3000° C have been used.
These high temperatures present severe, but not unsurmount-
able, apparatus limitations for extending the process to
much higher pressures, especially for producing large bodies.

Another important variation of the process that
allows unique fabrications features is hydrostatic- (or
isostatic-) pressure sintering. In this method the powder
is encapsulated in thin metal formed to the desired shape,
evacuated and sealed, placed in a pressure vessel, and then
pressurized by a fluid and heated. It is possible to pro-
duce shapes that clearly cannot be produced by the uniaxial
process. Pressures as high as 3 kbar at temperatures to
2200° C have been employed by workers at Battelle while
apparatus size and cost as well as safety present important
process limitations, the process offers capabilities unique
enough to justify it for certain applications.

3. MECHANISMS FOR PRESSURE SINTERING

Among the limitations of conventional sintering techniques are the difficulty in achieving full or sufficiently high density in some substances, and in restricting the grain growth that occurs at the high temperatures and the long times needed. Additives (aids) are sometimes used to help achieve densification and control grain growth. The additive often forms a liquid phase surrounding the grains and enhances diffusion during sintering. The control of grain size is important because it influences both the mechanical strength and the physical properties,(e.g., electrical and optical); generally the larger the grain size, the lower the strength.

Pressure affords an important variable for controlling the sintering process. By adjusting the pressure, temperature, time, and initial particle size, it is possible to control the final density and grain size to desirable levels. Fully dense, optically clear bodies have been produced from a wide range of different materials and often possess excellent mechanical and physical properties.

There has been considerable discussion of and speculation about the mechanisms involved in pressure sintering. It is doubtful that there is a single controlling mechanism. Rather, several phenomena come into play, including (a) diffusion, (b) plastic flow, and (c) atomic motion due to fracture and slip at grain boundaries. Particle rearrangement and packing is, of course, also

important in the initial stages.

It is generally agreed that diffusion is probably the controlling phenonmenon at low pressures. Some diffusion is always necessary to achieve some grain growth and bonding for material strength, but a balance between strength and grain size is often sought. Plastic flow aids in densification by removing voids and creates new "clean" surfaces for better bonding between grains. It becomes important, however, only after a critical pressure (different for each material) is reached. Fracture and slip also aid in achieving densification and creating new surfaces.

None of the above phenomena or the interrelationships between the various process variables (pressure, temperature, time, particle size, etc.) are fully understood at present. Undoubtedly there will be differences between different classes of materials and the nature of the problem is such that many of these differences have to be sorted out experimentally.

4. APPLICATIONS

Present and potential applications of pressure sintering span a broad gamut of materials technology. Examples range from the familiar sintering of metal-metal carbides such as cobalt-bonded tungsten carbide to the more recent and much higher pressure sintering of diamonds. Some specific areas for which the potential of pressure sintering either has been demonstrated or appears promising are listed below.

a. Improved Dielectrics

These include materials with low dielectric loss, high dielectric strength, high dielectric constant, nonlinear response, stronger piezoelectric response, etc.

b. Optical Quality Ceramics

Fully dense, transparent ceramics have been made from a wide variety of substances. Such materials are finding applications as optical windows, radiation detectors, laser hosts, and electro-optic devices. Examples include MgO, Y_2O_3, CaF_2, Al_2O_3, $MgAl_2O_4$, and the more recently developed family of ferroelectrics consisting of lanthanum-doped lead zirconate-titanate (PLZT).[3] All of these have been produced with sintering pressures < 1 kbar. Al_2O_3 (Lucalox), ThO_2-doped Y_2O_3 (Yttralox) and $MgAl_2O_4$ (Spinel) can also be produced by pressureless techniques. It now appears possible to make the PLZT's by conventional sintering also. These materials, however, were made first and are still being made by pressure sintering. Optical quality, undoped Y_2O_3 has been produced by pressure sintering only.[4] It is an excellent host for rare earth

ions and is transparent from 0.3 to 8μ. Single crystals can
be grown only in small sizes not suitable for many applica-
tions. The fully dense transparent material has transmission
characteristics which closely resemble those for the single
crystal and can be produced in relatively large (inch) sizes.

c. Electronic Materials

In addition to improving mechanical properties,
pressure sintering can be utilized to improve electrical
and thermal transport properties resulting in increased
lifetimes. An important recent development is the pressure
sintering of doped silicon-germanium alloys for thermo-
electric applications. Particularly pertinent is the obser-
vation that a modest increase in the sintering pressure
from 26000 psi to 28000 psi has resulted in marked improve-
ments in alloy homogeneity, mechanical strength, and
electrical and thermal properties.[5] The process, which may
also have important potential for other thermoelectrics
and for semiconductors, serves to illustrate that higher
pressures may be quite important for some materials.

d. Magnetic Materials

Structure-sensitive magnetic properties such as
the initial permeability, B-H characteristics, and lossiness
are affected by porosity, grain size, grain boundaries,
and inhomogeneity. Pressure sintering offers a means of
controlling the density and texture, and thereby the
properties, of polycrystalline and ceramic magnetic
materials. The process is particularly useful for
$MeO \cdot Fe_2O_3$ (ferrites) and $3Me_2O_3 \cdot 5Fe_2O_3$ (garnets), where
Me = transition metal, and, in fact, hot pressed ferrites

have been produced commercially. Furthermore, the lowering of the sintering temperature in pressure sintering can also be used to great advantage. In ferrites and garnets it is sometimes necessary to control the valence state of the transition metal ion to obtain desired properties and for some oxides and reactions this can be done only at relatively low temperatures, hence the advantage of pressure sintering.

e. Diamonds and Other Hard Materials

Recent work in the United States and Russia indicates that diamond powders can be sintered at high pressures. The process requires pressures up to ~ 60 kbar and temperature up to 2000° C and, in addition, the use of a sintering aid or binder. Many of the details have not been published and the best binders are not known, although small amounts (~ 1 mole %) of silicon, beryllium, or boron are known to help. This development has great technological implications for the machining and grinding industries in the making of pistons, dies, and cutting tools, etc. It is most likely that cubic boron nitride and other future super-hard materials can be sintered in a similar manner.

f. Refractory Materials

Many substances including oxides, carbides, borides, and nitrides cannot be sintered by conventional means, presumably due to the low atomic mobilities for diffusion even at high temperatures. Pressure sintering techniques have, however, been successful in yielding high-density compacts. Here higher pressures are generally needed because of the higher intrinsic strength of these materials.

g. Pressure Bonding

Pressure sintering can be used to bond similar
and dissimilar materials such as metal-metal, metal-ceramic,
and ceramic-ceramic. The strength and microstructure of
the bond can be made comparable to those of the parent
material. The isostatic process has much potential in
connection with bonding dissimilar materials and in
cladding and forming structural shapes. A good example is
the successful bonding of fine-grain alumina discs and tubes
to each other and to metal.

h. Composites

This is an area that can be expected to become
increasingly more important. It is becoming possible to
tailor-make fiber (wire) reinforced ceramic and metal com-
posites to meet certain strength and thermal expansion
requirements that cannot be met with the unreinforced
materials. Present techniques employ very modest pressures
(few thousand psi). Increasing the pressure range will un-
doubtedly open this area to a wider range of materials. Such
composites have applications as structural elements, and as
heat, radiation, and oxidation resistant materials.

5. IMPORTANT RESEARCH AREAS

Pressure sintering can benefit substantially from
further scientific and technological advances in the
following areas:

a. The Mechanisms for Sintering and Densification

Basic studies are needed, and emphasis should be
given to the interrelationships among the process variables
pressure, temperature, time, and particle size.

b. Processes of Plastic Deformation, Flow, and
Diffusion Under Pressure in Particular Solids.

The elementary question of why pressure lowers the
sintering temperature, involving these processes, has not been
answered broadly, although diffusion models have been developed[6]
for surface energy and applied pressure as simultaneous driving
forces. When diffusion transport is operative, these models
can account for the lowering of the necessary processing tem-
perature with applied pressure.

c. The Role of Inert Additivies (Sintering Aids,
Catalysts, etc.) and possibly Phase Transitions
on Contentional and High-Pressure Sintering.

More work is needed to understand the mechanisms
involved.

d. The Effects of Higher Pressure on the above
Variables and Mechanisms.

The recent observation that raising the sintering
pressure by < 10% greatly enhances the properties of thermo-
electric silicon-germanium alloys strongly emphasizes the
point. Extending the pressure range should open new possibil-
ities for sintering heretofore untried and difficult materials.
The recent successful sintering of diamond powders at pressures
in the 50- to 60-kbar range illustrates the point.

e. The Scale-up Problems associated with going to
Higher Pressures in both the Uniaxial and Isostatic
Pressure Sintering Processes.

Emphasis should be placed on finding suitable re-
fractory encapsulating materials and developing new and clever
recovery techniques. Present very-high-pressure apparatus
suffers from difficulty in recovering samples and the resulting
sample damage in the form of cracks and laminations. Early
results on materials sintered at very high pressures have

yielded low apparent mechanical strength, most likely result-
ing because of this damage. Thus, it is felt that the true
strength has not been measured.

 f. <u>The Use of the Isostatic Process to Fabricate
  Structures, Parts, and Components of a Single
  Material or a Composite of Materials</u>

  This process offers much promise and more effort
should be devoted to it and to extending its pressure
range. The possibility of forming complicated shapes by
this method also needs to be studied.

 g. <u>Automating or Semi-automating the Low-pressure
  Sintering Process</u>

  It is very doubtful that this could be done at
very high pressures.

ACKNOWLEDGMENT

  I wish to thank Dr. G. H. Haertling for valuable
references, suggestions and comments.

REFERENCES

1. T. Vasilos and R. M. Spriggs, "Pressure Sintering of
  Ceramics," in <u>Progress in Ceramic Science</u>, Vol. 4,
  edited by J. E. Burke, Pergamon Press, New York (1966).

2. R. M. Spriggs and L. Atteraas, "Densification of Single-
  Phase Systems under Pressure," in <u>Ceramic Microstructures</u>,
  edited by R. M. Fulrath and J. A. Pask, Wiley, New York (1967),

3. G. H. Haertling, <u>J. Am. Ceram. Soc.</u>, 54, 1 (1971); 54,
  303 (1971).

4. R. A. Lefever and John Matsko, <u>Mat. Res. Bulletin</u>, 2
  865 (1967).

5. R. A. Lefever, private communication.

6. R. L. Coble, <u>J. Appl. Phys.</u>, 41, 4798 (1970).

APPENDIX B

POWDER CONSOLIDATION

by S. H. Gelles
Battelle Memorial Institute

1. THE PROCESS

The consolidation of powder, whether metal or refractory compound, is usually accomplished in one of three basic ways. The first method is a cold-pressing operation usually involving a shaped die and high pressures (normally <100 ksi). This initial step is followed by a high-temperature sintering treatment which decreases the residual porosity in the compact and improves the mechanical and/or physical properties of the consolidated body. In the second method (hot pressing), pressure and heat are applied simultaneously to produce a body which usually has lower residual porosity than that from the cold-press sinter method. A combination of the two techniques (i.e., cold pressing followed by hot pressing) is also often used. The third technique, still in early stages of development, is that of explosive compaction. This process makes use of high explosives to produce the pressure for cold and, potentially for warm compaction.

The production of fully dense bodies from powders is dependent upon the ability of the powder particles to deform plastically by either glide or creep processes so that near intimate contact between adjacent particles is achieved. The degree of plastic deformation and, thus, the degree of interparticle contact is dependent on the powder particle-size distribution, purity, and the pressing

conditions of time, temperature, and pressure. Residual porosity is reduced or eliminated during heat treatment subsequent to cold pressing as a result of the operation of diffusion-controlled sintering processes. Such processes also occur during consolidation by hot pressing during which plastic deformation and sintering occur simultaneously.

Since it is thermally activated, the sintering operation depends on the time-temperature consolidation history with higher temperatures and longer times favoring the elimination of porosity and the strengthening of inter-particle bonds. The driving force for the sintering process is the reduction of surface energy and, therefore, is highly dependent on powder surface morphology, surface chemistry, and surface-defect structure. Certain impurities or additions to the powder surface sometimes contribute to enhanced or "activated" sintering (e.g., Ni or Pd additions to W) and provide fully dense bodies without pressure and at temperatures that are appreciably lower than those used in the hot-pressing process.

In conventional hot-pressing operations, pressure is generally not as sensitive a processing parameter as temperature with time at temperature and pressure being the least sensitive parameter. Hot-pressing pressures must be of about the same magnitude as the material-flow stresses at the processing temperature in order to produce the plastic deformation necessary for the intimate contact desired between powder particles. Pressure requirements can normally be reduced by increasing temperature. Thus, most metal powders

can be consolidated at pressures of about 1 to 5 kbars with
temperatures $>0.5_m$. There is an inherent trade-off be-
tween temperature and pressure with the usual result that it
is more economical to increase temperature and thus reduce
the flow stresses than it is to increase the pressure.
Increasing temperature also has the advantage of promoting
the sintering processes required for complete densification
and increased interparticle bonding. As an example of the
temperature-pressure trade-off, consolidation of beryllium
powder may be accomplished at 1100° C and 2000 psi or at
900° C and 10,000 psi.

Increased processing pressures would have an
advantage in the consolidation of very-high-melting-point
compounds whose flow stresses are very high even at
relatively high temperature. For these materials increases
in both temperature and pressure may provide a practical
solution to their processing. Explosive compaction coupled
with moderate temperatures may also offer a reasonable
alternative for the consolidation of hard refractory
materials.

Very high pressures are necessary in the consoli-
dation of materials such as diamond powder which is unstable
at low pressures and elevated temperature. Even in this
case it is usually possible to take advantage of the
sluggishness of the decomposition which allows consolidation
to be effected at pressures somewhat lower than the trans-
formation pressure if processing is sufficiently rapid.

Cold consolidation of powders at very high pressures might also provide sufficient energy to the structure to produce recrystallization in the consolidated powder during a subsequent sintering operation. The resulting fine-grain size could lead to stronger more ductile products.

2. IMPORTANCE

Consolidation of powder materials into usable final shapes and into preforms for subsequent operations such as forging is steadily growing in importance. It has been found to be an economical process for producing complex small parts directly to final shape and dimensions. Gears, sprockets, etc., produced from iron and iron-alloy powders are examples of this type of part. More than),000 tons of iron powder are consumed per year in such applications. The number of parts from copper- and aluminum-base metals is also growing, and growth is expected in the processing of titanium alloy and superalloy powders.

When produced by consolidation from powders, certain materials such as beryllium and some types of tool steel have mechanical or physical properties which are superior to those produced by the more conventional cast and wrought route. Cylindrical pressings of these materials as large as a few feet have been produced.

For refractory materials such as high-melting-point metals, ceramics, and the so-called hard metal compounds such as the metallic carbides, nitrides, and borides, the most practical method of producing usable bodies is often through powder-consolidation techniques.

Processing of these materials requires relatively high
temperatures because of their high melting points and
relatively low diffusion coefficients and, in the case of
the compounds, their lack of adequate low-temperature
deformation systems. In spite of the high temperatures
used, full density often is not achieved in these high
melting materials. Application of higher pressure to this
problem may achieve noteworthy results.

3. STATUS AND LIMITATIONS OF PROCESSES AND EQUIPMENT

The techniques and equipment used in the
consolidation of powders by cold pressing and sintering or
by hot-pressing operations have developed rapidly during
the past few years. For example, manufacturing presses
used in the cold compaction of powders have grown in
capacity from the 100-ton to the 1500-ton range. The size
and complexity of parts have also increased.

The cold-isostatic-pressing technique in which
powder is packed into an elastomer container, sealed,
and subjected to a fluid pressure has also developed
significantly. Batch processes are conducted in autoclaves
as large as 5 ft in diameter by ten ft long. Blocks of ceramic
17-in by 23-in x 116-in have been pressed in such equipment.
Other cold isostatic equipment 2 ft in diameter by 8·ft long
exists and is capable of pressures to 80,000 psi. This unit
has been used for the green pressing of large beryllium
bodies in preparation for hot-isostatic pressing. Research
is now underway in automating such equipment so that it may
be used for large production items. Experimental equipment

is also available (approximately 6" in diameter and 6" long) for cold isostatic pressing of powders in the 10 to 15 kbar range. Insufficient work has been done, however, to determine whether cold pressing with this apparatus at these pressure levels offers meaningful advantages. Theoretically, more intimate interparticle contact would be possible and would be accompanied by larger amounts of plastic deformation. The resulting increase in internal energy would enhance the sintering process and promote recrystallization during the post-pressing heat treatment thus leading to a fine-grain product.

Conventional hot pressing, usually carried out with graphite tooling, has been used to consolidate various intermetallics, refractory carbides, oxides, and metals. The technique is limited in operating pressure range to 2000 to 12,000 psi depending on the hot pressing size, by the tooling material, and it is often difficult to achieve full density under these conditions.

Hot-isostatic-pressing techniques in which a cold consolidated mass of powder is sheathed in a metallic container and subjected to a high gas pressure and elevated temperature have rapidly developed in the last few years. The process has produced large and complex shapes up to 2 ft in diameter and 5 ft long. The largest autoclave unit presently in operation has a 3-ft inside diameter and 9-ft inside length and can operate at pressures up to 15,000 psi. An autoclave 5 ft in diameter and 15 ft long operating in the same pressure range is now on the drawing board. Smaller autoclaves operating at higher pressures

(up to 150,000 psi) are available but only limited work has been performed especially at the higher pressures. The application of higher pressures in the consolidation of refractory compounds and metals would offer some advantages, but temperature limitations are presently imposed by the requirement for a ductile nonreactive sheathing material. Very little work has been performed on extending the pressure and temperature range of this process to consolidate refractory compounds to full density.

Some work has been conducted in the 20-to-70-kbar pressure range, and refractory borides, $SmCO_5$ and diamond powder are examples of the powders consolidated. Powder compaction at these very high pressures is still experimental and the amount of material that can be processed at a given time is very limited. Because of limited experience in this area, evaluation of the properties of the consolidated material has been largely neglected to date.

Explosive compaction of powders is another area that has received only limited attention in spite of the potentials of the process in regard to size and economy. The major problem area is the cracked compacts that often result from the process. Research efforts in sample design and in charge fixturing and detonation configuration coupled with the application of elevated temperature processing should lead to progress in the development of the process. The sintering of explosively compacted powder should be accelerated due to the relatively high energy imparted to the powder particles during compaction. Once again recrystallization could lead to a fine-grain structure having superior properties.

Finally it should be noted that relatively little work has been done in the area of surface morphology and chemistry and their effects on consolidation of powder. This is a very important field since these surface characteristics sensitively affect interparticle bonding and sintering processes. They are especially important in closed systems at high pressure where gas evolution as a result of adsorbed layers or impurity reactions involving gaseous products lead to high interparticle gas pressure and prevent full compaction. The problem can often be solved by hot outgassing and sealing in a closed container. Efforts to consolidate powders at high pressure must be concerned with these effects. Similarly, sintering aids (alloying elements added to the powder) can activate powder surfaces so that sintering reactions that occur after cold pressing or during hot-pressing operations would take place at lower temperatures. The reactions involved, however, are not too well understood.

4. RESEARCH RECOMMENDATIONS

Listed below are areas relating to the application of high-pressure technology to powder consolidation and visa versa that show promise of leading to scientific or technological advances in both areas.

a. Explosive Compaction of Powders

This area of our technology has not received much support although the potential benefits include economical powder compaction and consolidation of powders heretofore difficult or impossible to compact by other means. Exploration of warm or hot explosive compaction or cold compaction

followed by hot pressing or sintering are some of the areas
that appear fruitful.

b. Diamond and Hard Refractory Compound Powder Consolidation

The successful consolidation of diamond powder
and other refractory and wear-resistant materials could
contribute significantly to technology. These materials
could be used effectively in grinding or drilling tools and
in dies such as those used in the drawing of fine wire.
Diamond powder consolidation and fabrication into ultra-
high-pressure (megabar range) chambers would allow the
exploration of new forms of matter such as metallic hydro-
gen. Here again the use of explosive compaction might be
of benefit although other techniques such as the use of
sintering aids or special powder-surface preparations may
help in the consolidation and powder-bonding processes.

c. Intermediate Pressure Consolidation

It is within the present state-of-the-art to build
relatively large hydrostatic equipment (1 ft. in diameter
and several feet long) capable of operating in the 10- to
15-kbar pressure range. Such equipment would greatly
extend the present usual range of operating pressures for
powder compaction and would be useful in the consolidation
of refractory metals and ceramic materials. The higher
pressure levels should allow compaction at lower tempera-
tures and should produce materials with higher densities
and improved properties. The materials thus produced would
be of practical size and could in some cases be pressed to
near-finished shape and dimensions. Solid-state bonding of

difficult-to-join materials may also be feasible by the application of the increased pressure. Research efforts in this area should be fruitful.

d. Material Deformation at High Pressure

Studies of the deformation of materials under high pressure would be helpful in determining the desired temperature and pressure conditions for powder compaction. Information on the temperature and pressure dependencies of flow characteristics and their variation with crystal structure is the type of information that would be useful.

APPENDIX C
DYNAMIC HIGH-PRESSURE APPLICATIONS

by George A. Samara
Sandia Laboratories, Albuquerque, New Mexico

A great deal of progress has been made during
the past 20 years in studying the response of solids (and
some fluids) to shock-wave compression. Much of the work
has been motivated by military needs, but the results have
been of scientific as well as applied interest. The shock
method has many unique capabilities, very important among
which are the ability to attain very high-pressure high-
temperature states of matter not possible by present static
high pressure means and the ability to study the elastic
properties of solids over a large range of strain.
For example, germanium has a Hugoniot elastic limit of over
40 kbar and that of sapphire can be over 200 kbar along
certain crystallographic orientations.

Shock-wave research has made important contribu-
tions, particularly noteworthy are those in areas of
high-pressure equation of state and polymorphism of solids.
In addition, advances have been made in a number of other
areas: including (1) dynamic yielding and the interpretation
of elastic-plastic phenomena in terms of dislocation
dynamics, (2) material strength and fracture (spallation),
and (3) the electrical and magnetic response of certain
classes of solids (e.g., quartz, germanium, and iron alloys).
In most of the above areas results of carefully planned
and detailed experiments are just beginning to appear and

much more work needs to be done before sufficiently quantitative models of the phenomena can be devised.

The objective of this brief appendix is not to deal with the above aspects of shock-wave (or dynamic) high-pressure research but rather to focus on a few specific applied areas.

Certain aspects of dynamic high-pressure work are finding important applications in and hold substantial further potential for metals and metals fabrication technologies. These are explosives operations and can be divided into (1) explosives bonding, (2) explosives forming, and (3) shock-wave hardening.

These operations have proven to be useful in metals work, and in some instances, for example the bonding of incompatible metals, they are the only means feasible for performing the job. This is not to say, however, that these are a cure for all difficult metals operations; rather, they complement and/or compete with existing fabrication methods. Such operations are most advantageously exploited in applications not economical using conventional means and in applications requiring the production of limited quantities.

A body of information on these operations exists in the literature and a fairly up-to-date review of the field can be found in the references cited at the conclusion of this appendix. Only general remarks on these operations, their potential, and problem areas that need further investigation will be made here.

1. EXPLOSIVE BONDING: WELDING AND CLADDING

These are commercial operations used to bond metals together. Many different combinations of metals such as bismuth-steel, aluminum-titanium, aluminum-steel, copper-molybdenum, and zinc-zinc have been successfully bonded with this technique and it should be applicable to most combinations of metals. By conventional methods it is often difficult or impossible to bond dissimilar metals, such as metals with widely different melting points (e.g., bismuth-steel and lead-tungsten). In explosive bonding melting is not a requirement, and further-more, the process does not appear to be strongly influenced by large differences in the elastic and plastic properties of the metals. In fact, melting is not desirable since recrystal-lization and the possibility of formation of compounds and alloys at the interface between the two metals can lead to a weaker bond. Clearly then, explosive bonding is an important process. It generally has been applied for bonding simple geometrical shapes such as flat plates and cylindrical sur-faces; more complicated shapes are more difficult but may be possible.

The process is illustrated schematically as shown:
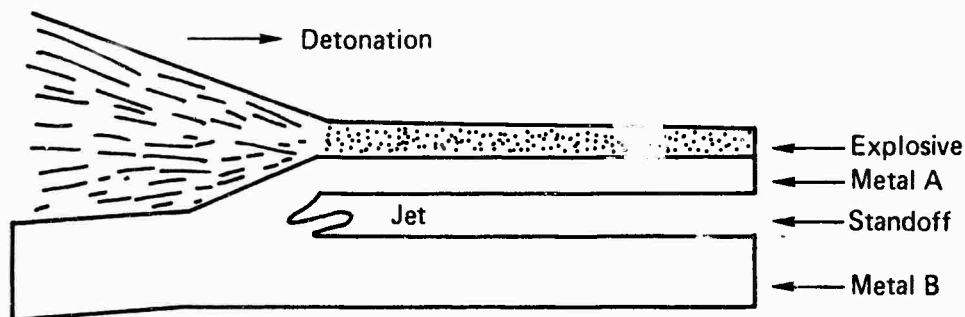
The two metals to be bonded are placed a small stand-off
distance apart. On detonating the explosive charge the upper
metal plate is driven downward at high velocity to collide
with the lower plate at a small angle. An explosive is
usually selected that detonates at a velocity which is lower
than the sound velocities in the metals. The collision point
will then traverse the metal surface at a subsonic speed and
permit jet formation upon collision. The colliding surfaces
contain oxide layers and other contaminants which are peeled
off by the jet which scours and exposes clean metal surfaces
as it moves forward. The clean surfaces behind the jet are
then forced together by explosive pressures in the tens to
hundreds of kilobars forming a bond (or weld). The forma-
tion of clean surfaces is an essential step in the bonding
process. If properly done, the resulting bond is mechanically
stronger than the weaker of the two metals. The strength of
the bond depends on a number of factors such as the pressure
and temperature conditions, crystallographic misorientation,
and the possible occurrence of melting at the interface.
Desirable conditions have to be determined for different
combinations of metals.

The mechanism by which explosive bonding is
achieved is not fully understood. Most hypotheses to date
are based on results of post-mortem analyses with no in-
situ data. Some of the mechanisms that have been postulated
include (a) fusion bonding, (b) cold pressure friction
bonding resulting from the relative sliding motion of the
two interfaces, and (c) bonding due to the jetting action
that occurs under oblique high velocity impact. Most
workers in the field favor the latter and this is

supported by post-mortem metallurgical examinations of
interfaces which often reveal strong evidence for jetting.
The two types of interfaces observed are (a) a straight
interface resulting from the direct bonding of the two
clean surfaces produced by collisions at large angles of
incidence, and (b) a wavy interface resulting from oscillation
in the jet flow and produced by collisions at small angles
of incidence. The details of the wave formation are also
not understood, but a qualitative explanation has been
advanced by Crossland and co-workers. It is speculated
that after detonation of the explosive the metal in contact
with the explosive moves ahead of the other and a metal
"tongue" from it penetrates the slower metal. This raises
a tongue in the second metal ahead of the collision point
and this tongue penetrates the first metal and the process
continues. In the absence of any direct in-situ observa-
tions it is difficult to be sure how closely this descrip-
tion reflects the actual phenomenon. Evidence for small
pockets of melting and solidification near the vortices of
the waves has been noted. Under conditions of very-high-
pressure collisions, these pockets coalesce to form a
continuous cast interface -- often an undesirable situation
resulting in a weaker bond.

Explosive cladding has been used to bond
metals to make coins and holds considerable promise for
forming speciality composites for wear-, erosion-, and
corrosion-resistant applications and, possibly, metal
composites suitable for high-temperature applications.
Plates up to ~300 ft^2 and cylindrical shapes of various
sizes have been successfully clad. The welding process
has been used for joining difficult dissimilar metals such

as aluminum-steel for marine applications and for welding
tubes to tube plates in heat exchangers, condensers, and
boilers, particularly in nuclear power generators. It has
been speculated that the latter process may replace the
conventional tube-expansion methods.

2. EXPLOSIVE FORMING

As opposed to explosive bonding in which dynamic
pressures of tens to hundreds of kbar are needed, explosive
forming is a relatively low-pressure process requiring
pressures on the order of only several thousand psi. The
pressure is generated by an explosive charge set off some
distance away from the metal-form die combination and trans-
mitted to the metal via an inert medium, generally water.
The metal flows (stretches) to the desired form.

Explosive forming has proven to be economically
sound and competitive for certain metal fabrications and,
in some instances, is superior to conventional processes.
Among its strong features are its ability:

a.   To meet close dimensional tolerance require-
ments on both small and large objects;

b.   To form nonsymmetric and unusual shapes (such
shapes are often very difficult to produce by conventional
means, but become easy by the explosive method after a form
die is made);

c.   To form large workpieces;

d.   To utilize dies of low-cost materials when
production quantities will be small;

e.   To allow quick response time; and

f.   To form metals that are difficult to form by
conventional means.

The formability (ultimate elongation) of most metals is not

markedly changed by the high strain rates involved in explosive working, and the residual metallurgical properties usually are comparable to those following cold working to a similar level of deformation.

3. SHOCK-WAVE HARDENING

This has long been recognized as a useful metal-working process and has been employed in the surface hardening of rails and crusher jaws. Conventional processes require large plastic deformations to achieve needed hardness, while, on the other hand, the same results can be achieved with very little deformation under the very-high-strain-rate conditions of the dynamic process. Pressures in the 10 to 100-kbar range are involved and the hardness decreases with increasing depth into the object. The process does not appear to be widely used at present but it may have potential applications in wear-resistant and structural materials.

Both the shock-wave-stress amplitude and duration affect the residual hardness and microstructure of the material. A low-amplitude pulse of long duration can be as effective as a higher-amplitude pulse of shorter duration. The hardness of metal is thought to be determined by such factors as the density of dislocations, stacking faults, and deformation twinning. Recent investigations of the shock hardening of Hadfield steel from 0 to 500 kbar have indicated that it is the dislocation density and not the specific microstructure that controls the hardness of this material.[4] Detailed studies of other materials are needed to establish if this is a general conclusion. Hadfield

steel, an austenitic manganese steel, exhibits an unusually large shock hardening effect. An increase in its hardness by as much as a factor of four in 200 kbar has been noted.

4. CONCLUSIONS AND RECOMMENDATIONS

Much technological progress has been made in recent years in explosive operations described above, and they are now recognized as competitive or unique metalworking processes. However, the mechanisms and nature of the phenomena involved are not sufficiently well understood. The energetics of explosive detonation and energy transfer to metal are reasonably well understood for high-density military explosives, but solution of such problems requires utilization of complex computer codes. Few industrial firms actively using explosive metalworking have the capability to perform such computations and, in fact, there has been no clear demonstration that such codes can indeed solve the design problems involved. Furthermore, performance data required by the codes are not available on the low-density, commercial explosive formulations most commonly used in metalworking applications. The rates, pressures, and temperatures achieved are important process parameters. All present knowledge about explosive bonding is based on post-mortem analyses. Direct observations and measurements are very difficult but sorely needed. Other important areas in need of research include those of metal plasticity and dislocation mechanics (as they affect flow and hardening) under conditions of very high strain rates. Some progress in these latter areas has been achieved in recent years but more remains to be done.

ACKNOWLEDGEMENT

REFERENCES

1. G. R. Cowan and A. R. Holtzman, "Flow Configurations in Colliding Plates: Explosive Bonding," J. Applied Physics, 34, 928 (1963).

2. B. Crossland, "The Development of Explosive Welding and Its Application in Engineering," Metals and Materials, 5, 401 (1971).

3. American Society of Mechanical Engineers, Proceedings of the Symposium on the Behavior and Utilization of Explosives in Engineering Design, March 2-3, 1972, Albuquerque, New Mexico.

4. A. R. Champion and R. W. Rohde, J. Appl. Phys., 41, 2213 (1970).

APPENDIX D
HIGH-PRESSURE TECHNOLOGY

by H. M. Strong
General Electric Research & Development Center

1. INTRODUCTION

Since 1955, pressure has become a readily
available and powerful thermodynamic variable in the hands
of possibly 2,000 to 3,000 workers throughout the world.
That so many should be thus engaged when so few profitable
products, only two in fact, have been discovered may seem
surprising until one realizes that an incentive even more
powerful than product is curiosity. High pressure has
served well in this respect; as a newly available thermo-
dynamic variable it has offered many answers, many surprises,
and many new questions. In addition, it has resulted in
some metal working at 10 to 20 kbar, some sintered things,
a couple of hard abrasives and interesting organic reac-
tions, but no polymer products. At 60 kbar, the volume
available is still much too small for superalloy or polymer
parts.

Not many technologically important products can be
expected in view of the present state of the art. The
volume is too small, and only a few pressure-generated
materials have any permanence after pressure is removed.
Thus, what can be made or modified and does have permanence
must find its place in technology in the form of small
pieces--a few cubic centimeters. For the rest, pressure
remains a pry for opening mysteries, such far-off mysteries
perhaps as where lies metallic carbon, metallic hydrogen,

and metallic some other things. These are problems of
the greatest technical difficulty and may demand static
pressures of 1 to 6 megabars which severely strains
pressure capabilities.

In this appendix an attempt is made to illustrate
how pressure is achieved and to describe its principle
effects on matter. To enumerate all its effects is an
impossible undertaking; however, it is possible that from
the vast literature on the subject, an imaginative person
might find a few resources for generating novel solutions
to specific problems. Most of the work accomplished to
date seems to have been an effort to add to the expanding
list of new forms of matter, new phase lines, new resistance
phenomena, new curie points, new superconductors, etc.
There might be virtue now in trying to discover whether
there are useful properties for specific needs among all
these stored treasures. The sort key may be an imaginative
theoretical scan of what already exists.

2. APPARATUS

The real-life facts about high-pressure appara-
tuses are that they are expensive, their useful lives are
relatively short, and their reaction volume is small.
All of these factors become exponentially more unfavorable
to man's purposes as the pressure demand increases. For
this reason, any technologically useful product of high
pressure made at 50 kbar, for example, must have an economic
value of $4,000 to $5,000 per lb. This economic limit will
go up or down as the pressure required increases or decreases.

All apparatuses for pressures exceeding about 40 kbar require massive support for the regions of most intense stress. Consequently, the machinery for applying the force must have capability for generating both the supporting forces as well as the compressive force. The ratio of total force to compressive force increases from approximately 2.0 at 40 kbar to 10 at 100 kbar for apparatuses capable of many excursions to high pressure.

While the designs and adaptations of high-pressure apparatuses differ in many details, the basic principles of design do not. All have evolved from the Bridgman piston and cylinder or anvil apparatuses through the Drickamer anvil, GE belt, or VonPlatten sphere into a proliferation of styles that employ Bridgman's principle of "massive support" to the regions of greatest stress.

It is comparatively easy to build an apparatus to perform a few laboratory experiments and quite another to build one with such exquisite perfection that it becomes a production machine. Thus, one is likely to read of performance claims that have not been tested thoroughly in everyday work.

The useful reaction volume at 20 kbar may be several cubic centimeters, but at 50 kbar the volume drops to around 1 or 2 cm^3. At 150 kbar, one may be limited to match-head-size experiments, about 15 mm^3. Naturally, the volume available is dependent also on the temperature that must be applied, and the volumes quoted above apply when temperatures over about 1000° C are used. At low

temperatures, the space needed for internal thermal insulation can be reduced and the working volume increased.

The illustrations (Figures 1 - 10) and descriptions of apparatuses that follow are intended to give a picture of the several types now said to be in use throughout the world.

The basic construction materials of high pressure equipment are high-grade steels for supporting rings and massive backup blocks, and cemented tungsten carbide with 1 to 6% cobalt for pistons and chambers. The strengths of several types of construction materials are given in Table 1 below.

TABLE I

Properties of Materials Useful in High-Pressure Construction

Material	Avg. Strength (kb)		Avg. Young's Modulus (kb)
	Compression	Tension	
Steel, 18-8 stainless	5-10	5-10	2000
Steel, 4340 or maraging	15-25	15-20	2000
Cobalt-cemented			
Tungsten carbide			
3% Co	60	11	6500
6% Co	45	14	5600
13% Co	40	22	5300
Beryllium copper	12	12	1200
Glass fibers, laid			
parallel in resin	6	10	380
Boron fibers, laid			
parallel in resin	10	20	4000
Single graphite fibers	–	25	4500
Sapphire	40	–	3500
Diamond	120+	–	13000
Pyrophyllite	1	0.1	800
NaCl	0.3	–	400
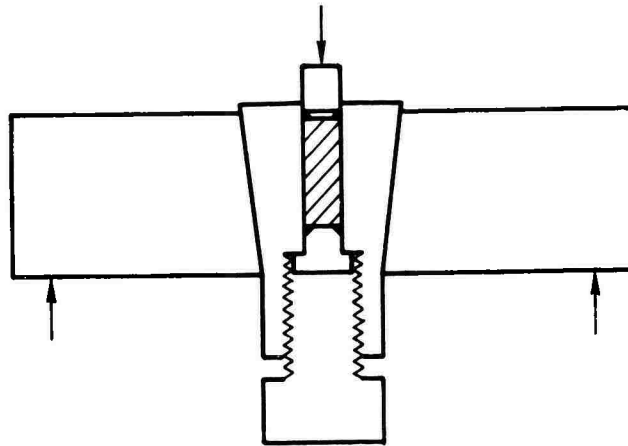
FIGURE 1   Progressive internal and external loading
of pressure cylinder.

Pressure limit: about 40 kbar--for 1-5
excursions

Piston diameter: about 1/2 inch maximum

Piston material: tungsten carbide

Reproduced from: P. W. Bridgman, "The Physics of
High Pressure," (London: G. Bell and
Sons, Ltd., 1958).
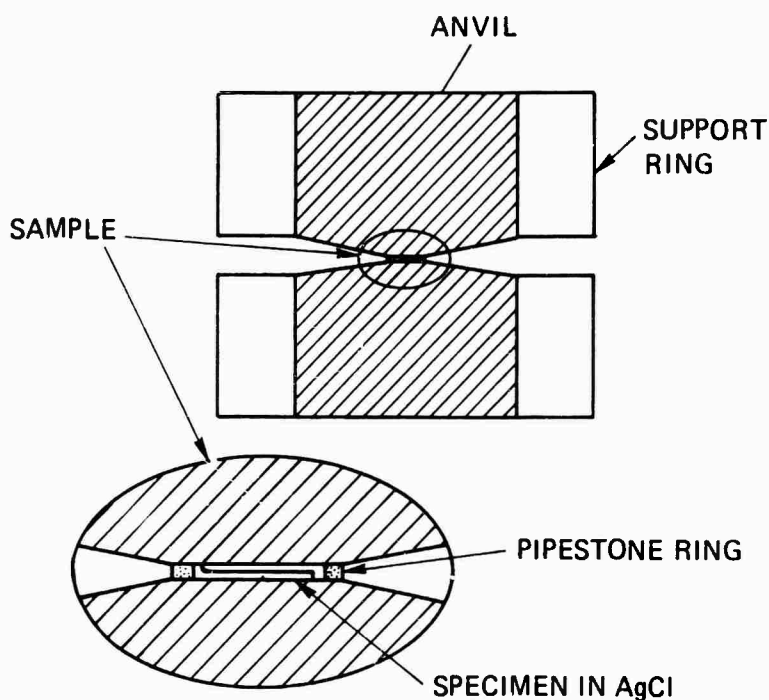
FIGURE 2.   Opposed anvil apparatus of P. W. Bridgman

Pressure limit: about 100 kbar for a few
                  excursions
Anvil material: tungsten carbide

Anvil diameter: about 1/2 inch, thickness,
                  0.010 in.

Reproduced from: P. W. Bridgman, Proc. Am. Acad. Arts and
                 Sciences, 74, 425 (1942).
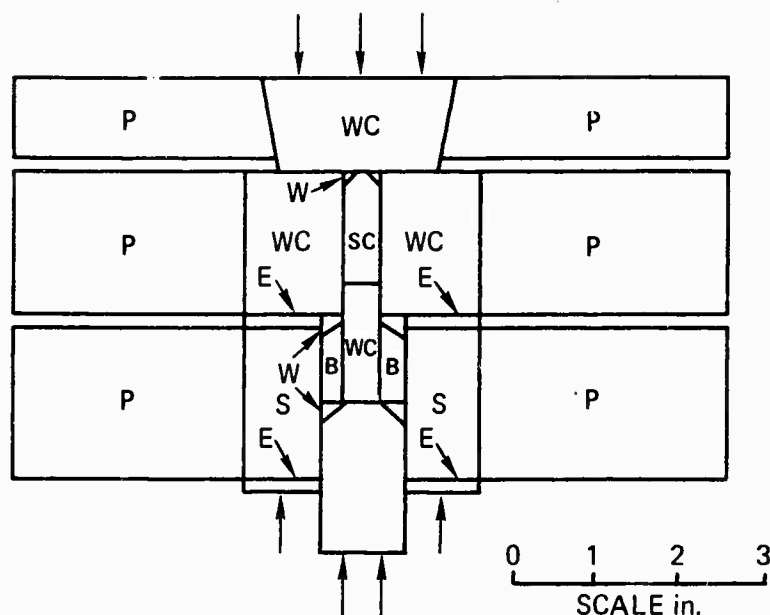
P   = HIGH PRESSURE "PLATE" OR
      SHRINK-FIT CONTAINING RING
WC = TUNGSTEN CARBIDE
S   = STEEL
E   = STEEL END—LOAD RING
SC = SAMPLE CHAMBER
B   = BISMUTH METAL
W   = STAINLESS STEEL WASHER

FIGURE 3.   Double-staged piston-cylinder apparatus.

Piston has flank support through pressurized Bi

Pressure limit: 60 kbar

Piston diameter: 1/2 inch

Reproduced from: A. Jayaraman, W. Klement, Jr., R. C. Newton,
and G. C. Kennedy, "Fusion Curves and Poly-
morphic Transitions of Group III Elements -
Aluminum, Gallium, Indium, and Thallium -
at High Pressures," J. Phy. & Chem. Solids,
24, 7 (1963).
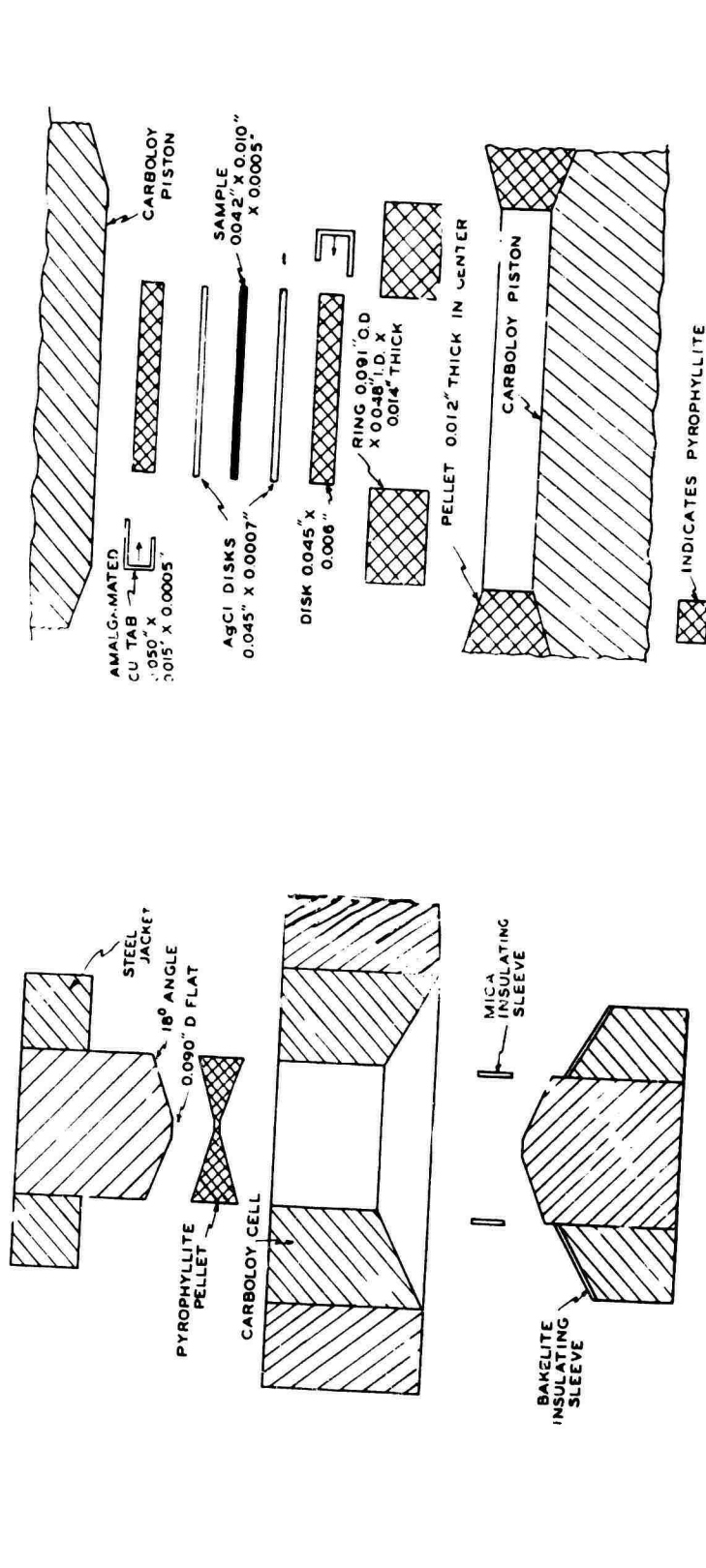
FIGURE 4 (a) Very high-pressure anvil apparatus of H. G. Drickamer

FIGURE 4 (b) Central high-pressure region of Drickamer anvils.

Pressure limit: about 300 kbar, 1-3 excursions

Reproduced from: A. S. Balchan and H. G. Drickamer, "High-Pressure Electrical Resistance Cell, and Calibration Points above 100 Kilobars," Rev. Sci. Instru., 32, 308 (1961).

* See Appendix E for evidence that pressures to 450 kbar have been reached.
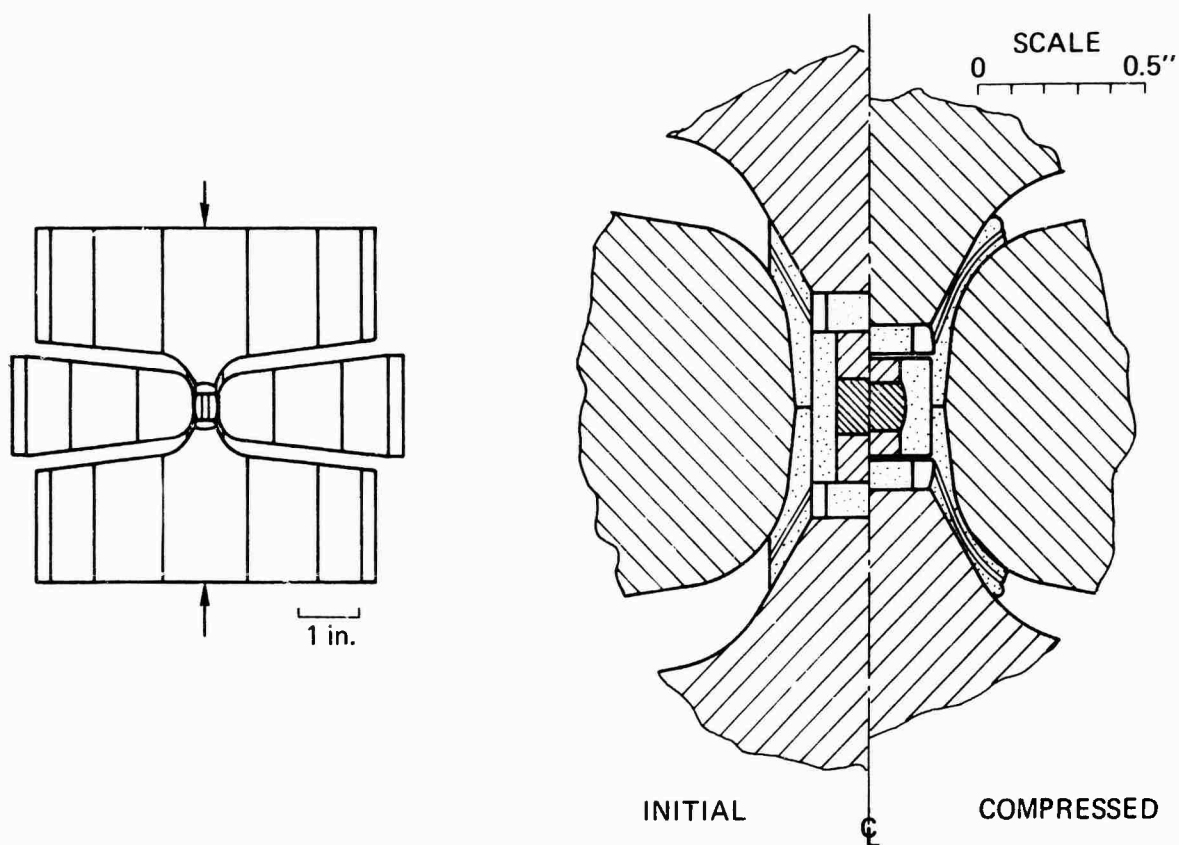
FIGURE 5(a)   Belt apparatus of H. T. Hall

FIGURE 5(b)   One side shown before compression: the
              other side shown at about 60 kbar.

              Pressure limit, about 60-70 kbar;
                        10 to 400 excursions,
                        depending on pressure applied.

Reproduced from: H. T. Hall, Rev. Sci. Instru., 31, 125 (1960).
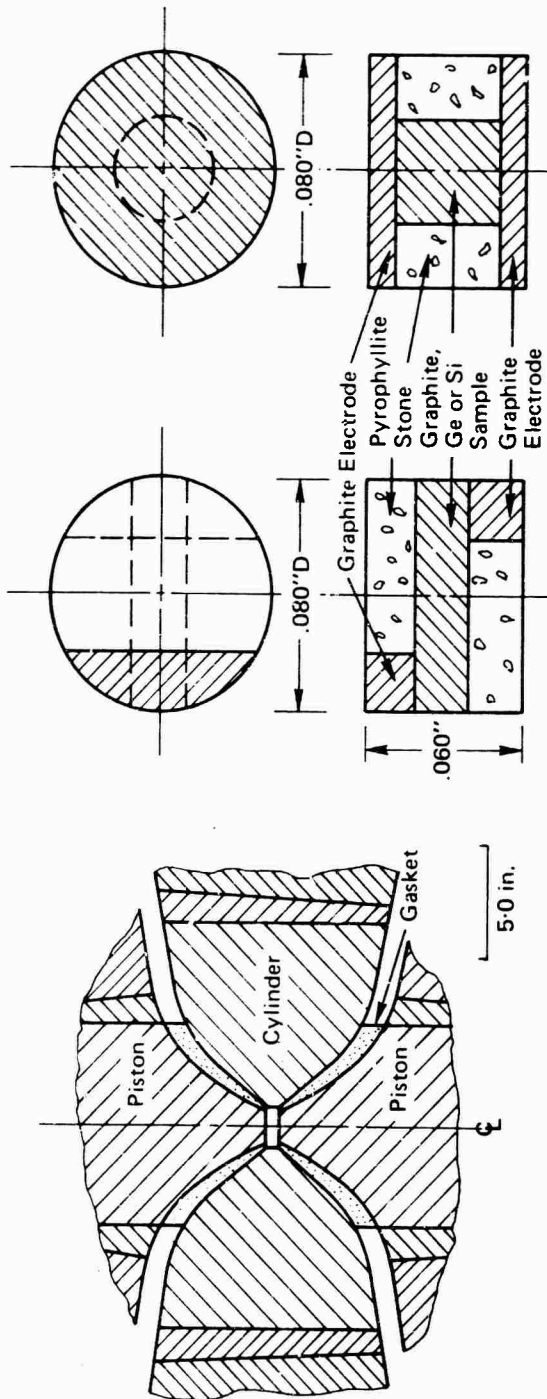
FIGURE 6(a)   High-compression "belt" apparatus of F. P. Bundy

FIGURE 6(b)   "Bar" samples and "spool" samples used in the high-
              compression "belt" apparatus.

              Pressure limit: about 200 kbar

              Heated volume: 15 mm^3

              Total volume: 150 mm^3

              Many excursions to high pressure possible.

Reproduced from: F. P. Bundy, J. Chem. Phys., 38, 631 (1963).
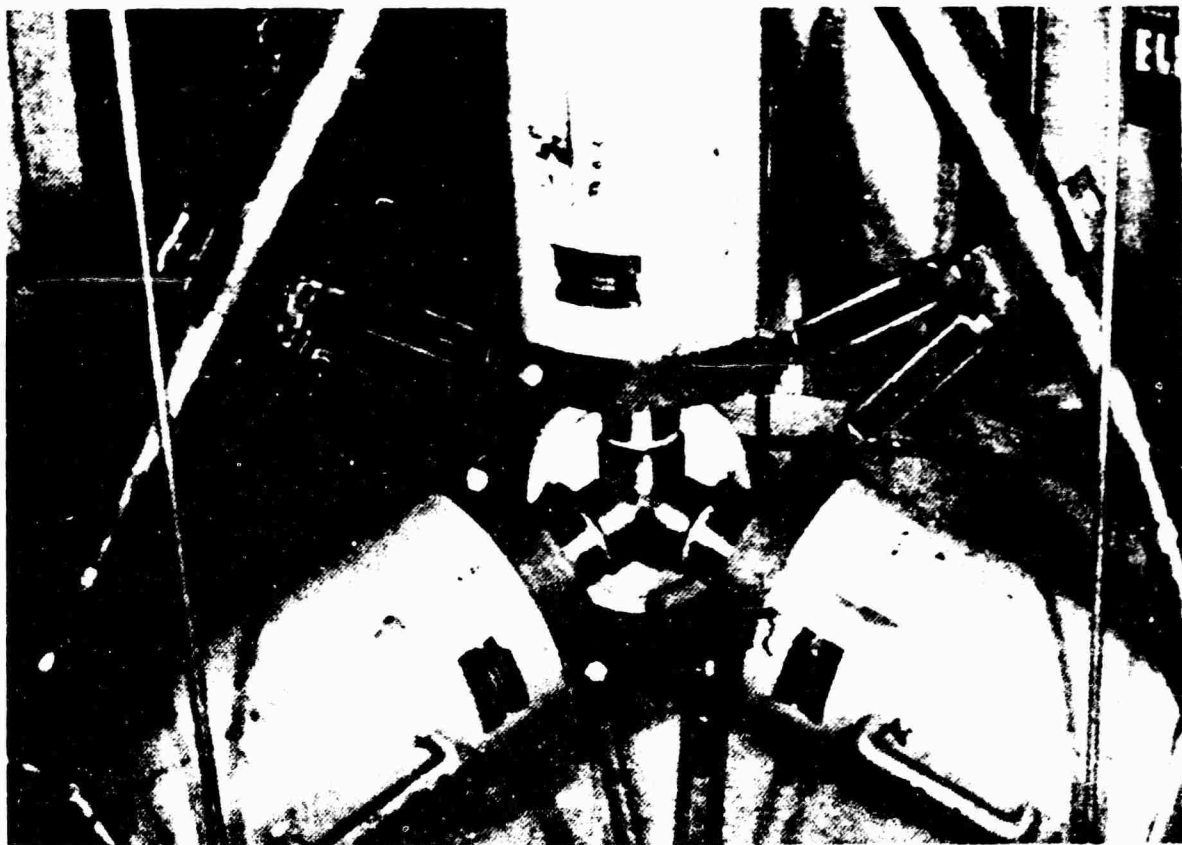
FIGURE 7(a)   Tetrahedral apparatus of H. T. Hall

Pressure limit: about 60-70 kbars;
                10 to 400 excursions,
                depending on pressure applied.

Anvil face: $\sim$1/2 - 1 inch

Reproduced from: H. T. Hall, Rev. Sci. Instru., 29, 267 (1958)
                        "   "   "   33, 1278 (1962)
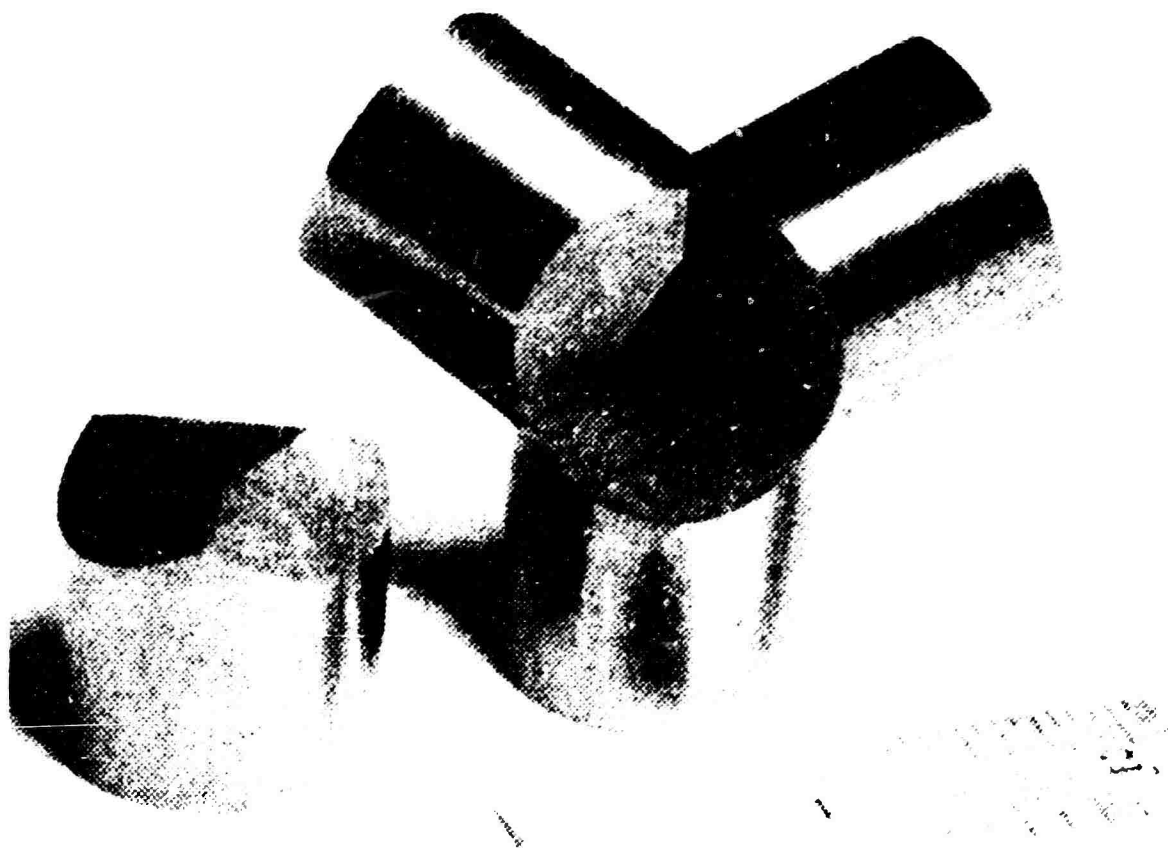
FIGURE 7(b)   Nest of tetrahedral pistons.

Pressure limit: about 60-70 kbar;
                        10 to 400 excursions,
                        depending on pressure applied.

Anvil face: ~1/2 - 1 inch

Reproduced from: H. T. Hall, Rev. Sci. Instru., 29, 267 (1958).
                           "   "   "   33, 1278 (1962).

Labels (top to bottom):
- Electrical conductor for heating current
- Vent
- Top cap of primary pressure vessel (6kb)
- Rubber liner to primary chamber
- Water to maximum pressure of 6 kb
- Electrical insulating sleeve
- Copper sheath around six-piston assembly
- Hard steel gasket
- Electrical insulation sleeve
- Graphite heater rod
- Reaction chamber
- Thermal insulation
- Copper sample holder
- Piston assembly in three layers
- Cylindrical primary pressure chamber heavily wrapped with steel wire under tension

Top platen of vertical restraining structure

VENT

Connection to high pressure water pump

Bottom platen

FIGURE 8   Von Platen's cube apparatus

Inner cube has 75 mm edge

Pressure limit: probably ~60 kbar

Reproduced from: J. Liander and E. Lundblad, "Some Observations on Synthesis of Diamonds," Arkiv. Kemi., 16, 139 (1960).
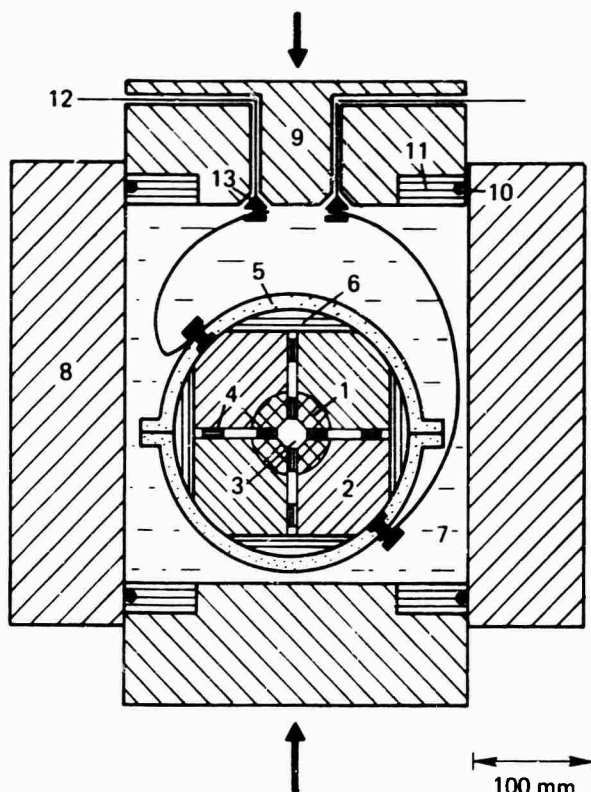
Single 8-anvil type split sphere apparatus in oil reservoir.
Only two of eight leads are shown here. 1—Tungsten carbide
anvil core, 2—steel backing block, 3—sample chamber, 4—
insulator sheet, 5—rubber shell, 6—corner cap, 7—copper
electrode, 8—cylinder, 9—piston, 10—O-ring, 11—nylon ring,
12—lead, 13—copper cone.

FIGURE 9   Kawai and Endo's split sphere apparatus

Pressure limit: probably >300 kbars

Reproduced from: N. Kawai and S. Endo, "The Generation of
Ultrahigh Pressures by a Split Sphere
Apparatus," Rev. Sci. Instru., 41, No. 8,
1178 (1970).
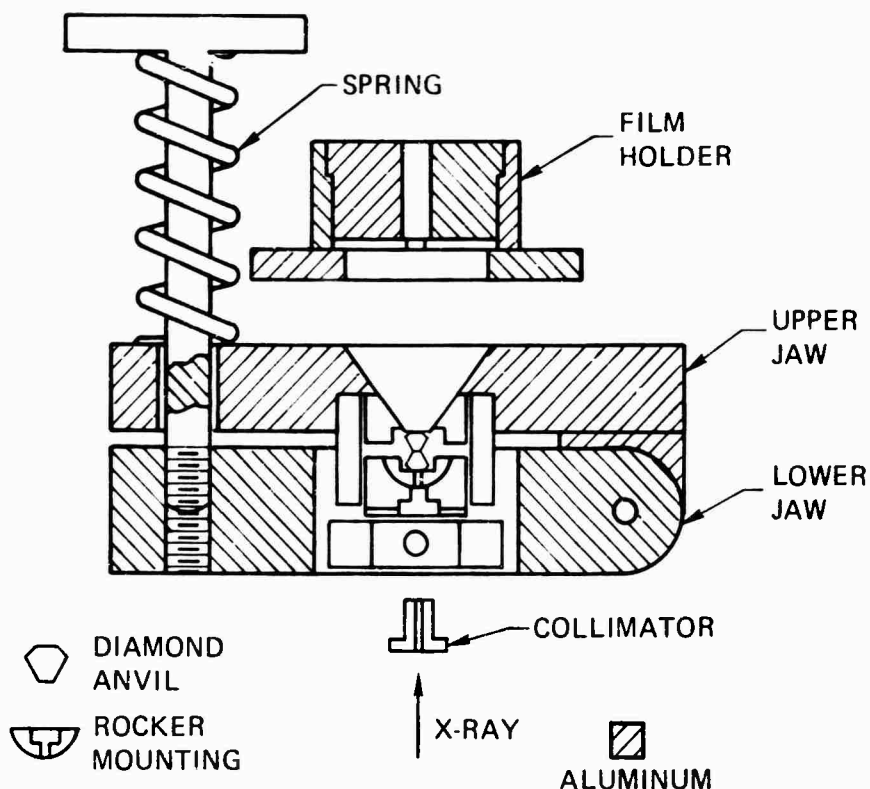
FIGURE 10 Diamond anvil apparatus for X-ray diffraction
at high pressure.

Anvil face diameter: 1 mm   0.3 mm

Pressure limit: ~200 kbars   ~300 kbars

Adapted from: C. E. Weir, E. R. Lippincot, A. VanValkenburg,
and E. W. Bunting, Bur. Stds., J. Res., 63A,
55 (1959).

T. Takahashi and W. A. Bassett, Science, 145,
483- 486, 31 July 1964. Fig. 1. (Copyright 1964
by the American Association for the Advancement
of Science.)

See also: Rev. of Sci. Insts., 38, No. 1, 37-42, Jan. 1967
and Scientific American, 212, No. 6, June 1965
pp 100-108, for newer designs.

The pressures attainable in a laboratory are in
principle without limit if one could increase the flank
support to the regions of highest stress (i.e., piston
tip and cylinder walls without limit). This corresponds
to Bridgman's principle of "massive support," but one
soon runs into unwieldy practical difficulties. The re-
action volume becomes very small in comparison to the
supporting structures; the available force budget is mostly
consumed in supplying the support, and one tends to lose
track of the pressure (P) actually being generated for the
reaction in terms of applied force. The proper balance
of flank support in relation to the piston face pressure
becomes very difficult to achieve as P increases.
In the present state of the art of applying flank support,
the practical upper pressure limit for studies at room
temperature was extended to about 300 kbar at very small
volumes. For pressurizing at high temperature, the
pressure limit presently is about 200 kbar.

The spherical apparatuses of VonPlatten and Kawai
may have some advantages in volume and pressure capability
over the more conventional piston or punch type since they
probably give a more nearly spherically symmetrical
distribution of st·ess than do other types. The proper
flank support may be automatically achieved, and the central
region, including the anvils, are more nearly hydrostati-
cally compressed. Kawai's apparatus has probably exceeded
300 kbar.

The spherical types seem better adapted to
scientific experiments than to routine production. Also,
in prolonged high-temperature work, the need for cooling
may be more difficult to satisfy.

Pressure apparatuses of the type illustrated
are adapted for using solid pressure transmitting media
(typically pyrophyllite) in which it is usually quite
difficult to obtain a hydrostatic pressure distribution.
A further complication arises when phase transformations
start; as the transformation runs there will be an internal
volume change that the apparatus may not follow. The large
frictional forces between the compression members and gasket
material as well as the rigidity of the pressure transmitting
medium may easily bridge over the pressure cavity at the
specimen when its volume shrinks, or it may contain the
extra pressure when its volume trys to expand as in melting.
Some alleviation of these problems is obtained when it is
possible to surround the specimen with softer materials
such as talc, silver chloride, lead, indium, or sodium chloride.

It is obviously not possible to use the simple
force-divided-by-area formula to calculate the pressure
on the specimen. Instead, a series of calibration refer-
ence points are used to calibrate internal pressure in
terms of applied force. These reference points are phase
transformations in the several elements listed in Fig. 11
(the former and 1970 revised reference points are given).
The transitions may be detected by one of the following:
(1) volume change; (2) electrical resistance change; or

CONVERSION TO NEW 1970 P SCALE   FPB: 5 Jan '71

H. G. DRICKAMER
Rev. Sci. Instr. *41*, 1667 (Nov. '70)

Decker, Hall
Drickamer

DRICKAMER HIGH P SCALE (1970)

Element	Old kbar	New kbar
Bi (3–5)	88	73–75
Fe (α–ε)	133	110–113
Ba (2–3)	144	118–122
Eu (1–2)	150–160	122–130
Pb (1–2)	160	128–132
Rb (2–3)	190	142–153
Cs (max)	170–180	133–142
Ca (max)	350–375	235–255
Rb (max)	420–435	290–320

Drickamer's
Old 1961 Scale

Bridgman
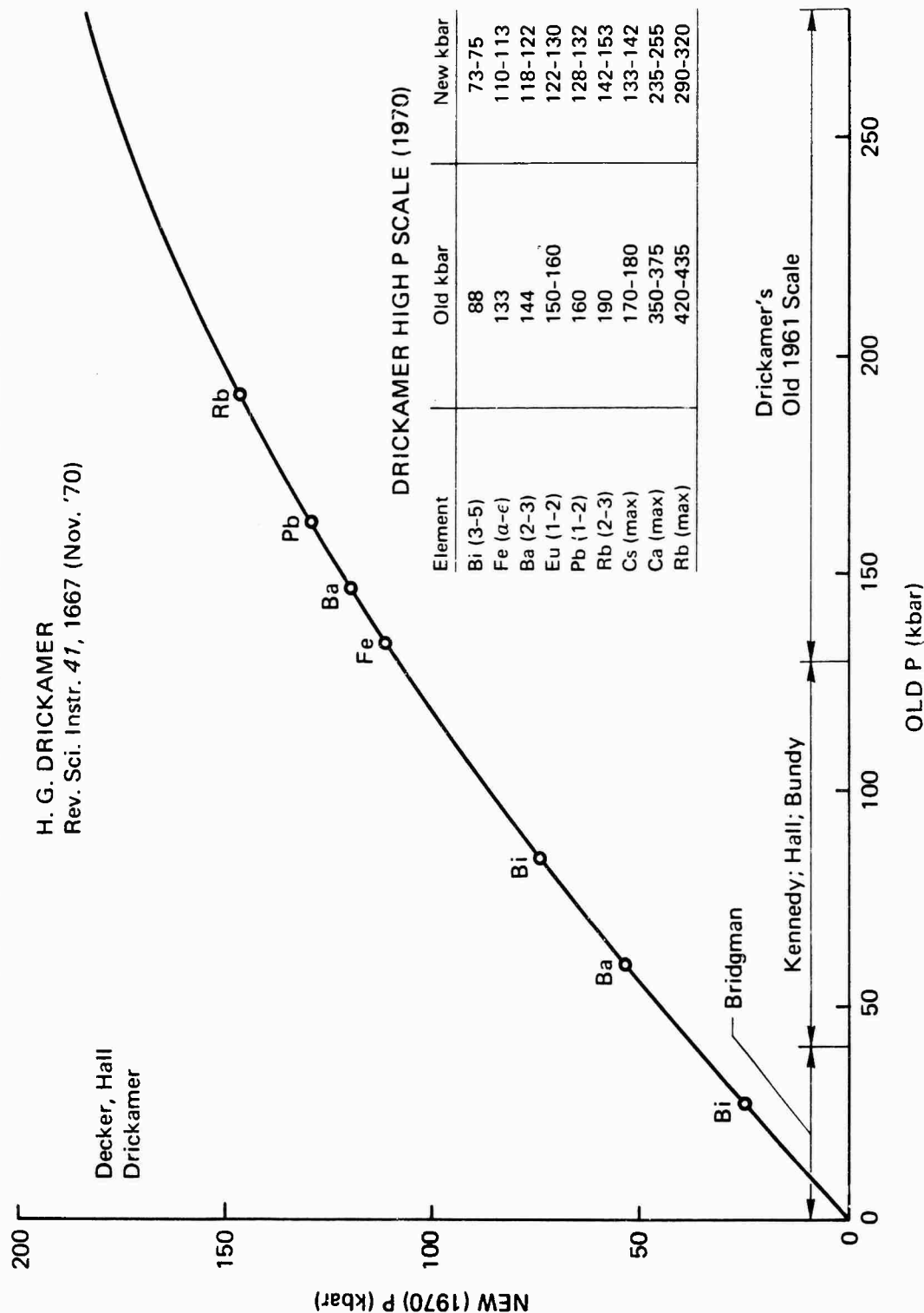
Kennedy; Hall; Bundy

OLD P (kbar)

NEW (1970) P (kbar)

FIGURE 11

(3) structural change (X-ray diffraction). The higher the pressure, the more uncertain is the exact pressure location for the reference transition.

When applying internal heating, the experimenter is beleaguered by a new set of complications. With increase of temperature, the internal parts at first expand increasing the pressure along some inexactly known pressure-temperature (P-T) path until some transformation occurs in specimen or pressure medium, after which the pressure changes rapidly. Talc and pyrophyllite are particularly troublesome in this respect, because at temperatures near or above 1300° C, these materials increase their densities abruptly by modifications in their aluminum silicate structures. Internal pressure decreases of as much as 10; 15 kbar have been noted in heated pyrophyllite media (Strong, unpublished data and (1962).

Thermocouples are almost always used to measure internal temperatures. This method works quite well, but for precise work (determining the slope of a phase boundary), one must recognize that thermocouples wander off in calibration as the pressure increases (Bridgman, 1918; Bundy, 1961; Hanneman and Strong, 1965; Getting and Kennedy, 1970). At prolonged high temperature dwells, it is rather common for the thermocouple to suffer chemical attack or contamination, with loss of accurate calibration.

It is clear then that the high-pressure experimenter will need to recognize several possibilities for error. Sometimes it is possible to approach the problem of measurement from more than one direction to improve reliability. For example: one may observe two phase transitions in the same experiment, one being a more or less established reference point; one may measure the compression of a standardized cell companion material such as sodium chloride; or one may be able to do the experiment in more than one type of apparatus.

The lifetime of a high-pressure apparatus is highly variable but generally short compared to apparatuses used in the 1-to 10-kbar range. Structural materials used are selected for their high compressive strengths and are generally quite brittle. Their breaking points are consequently quite erratic in terms of breaking tension and number of excursions to high pressure. But the skillful experimenter using a well-balanced design can obtain several hundred experiments in a 60-kbar apparatus.

Occasionally, one hears about new apparatus designs having unusual pressure and/or volume capability, for example, in the paper of Vereschagin et al. (1970), the possibility of a static apparatus capable of generating a pressure of 1 megabar is discussed. The anvils in this apparatus were to be made of diamond composite material having an elastic modulus of 60×10^{11} dynes/cm^2. This modulus is the same as that of cemented tungsten carbide. However, it was suggested that the modulus would reach 75×10^{11} dynes/cm^2, a calculated value, after the pores

were squeezed out of the composite under high pressure.
The matrix material was not described, but its elastic
modulus suggests that it may be tungsten carbide. A demon-
stration of 1-megabar capability has not been reported at
this writing.

Many high-pressure apparatus designs are available
for selection of one adapted to particular needs. All of
them depend for their success upon the principle of massive
support to regions of greatest stress. Theoretically, there
seems to be no limit to pressures attainable by extension
of the principle of massive support, short of a phase
transformation in the highly stressed portions of the
pressure anvils.

While most apparatuses described are limited to
a ~300 kbar pressure at room temperature and ~200 kbar at
high temperature, the spherically symmetrical design may
have a higher pressure limit. It may be that this latter
design can most easily be adapted to extending the pressure
range.

3. PHASE TRANSFORMATIONS

With the possibility of subjecting matter to a
wide range of pressures and temperatures, the variety of
new structures that can be experienced proliferates faster
than it can be reviewed. A goodly number of them have been
classified and catalogued by Klement and Jayaraman (1967),
Wentorf (1969), and Rooymans (1969), whose reviews were
a valuable aid in preparing this report.

The different phases of a substance (liquid,
crystal type, vapor) each normally have sharply bounded
definite regions in p and T space for thermodynamic
stability. At a boundary line, two phases are in
equilibrium in the sense that the Gibbs free energies,
G, of the respective phases are equal, where $G = U-TS +pV$;
U is the internal energy, T temperature, S entropy, p pressure,
and V volume. For an infinitesimal variation, $dg = V\, dp - S\, dT$, and, along the i - j equilibrium-phase boundary,
$dG_i = dG_j$. This leads to the Clausius-Clapeyron equation
for first-order transformations,

$$\left.\frac{dT}{dp}\right|_{i-j} = \frac{V_j - V_i}{S_j - S_i} = \frac{\Delta V}{\Delta S} \, ,$$

It is convenient to express dT/dp in degrees/kbar, in which
case,

$$\frac{dT}{dp} \text{ (in °/kbar)} = 23.9 \frac{\Delta V}{\Delta S} \quad \begin{array}{l}\text{(in } cm^3/\text{g-atom)}\\ \text{(in cal/g-atom° or}\\ \text{entropy units, eu).}\end{array}$$

This defines the direction of the boundary line between the
two phases i and j in pressure and temperature space at any
p and T for which ΔV and ΔS are known, usually zero pressure.
In order for a transformation to proceed across the boundary
line from i to j, it must have thermodynamic permission to
do so -- specifically, $G_i > G_j$. In many reactions, the
application of pressure is a requirement for tipping the
free energy balance in favor of j. The energy supplied to the
system by pressure is $p\Delta V$ and is usually little more than
a few hundred calories to one kilocalorie/mole in high-

pressure condensed-state reactions. Because solids are
relatively incompressible (ΔV small), p must be large to
generate even this small energy.

Most phase boundary lines are more or less curved.
This curvature results from shifts in relative compressi-
bilities, thermal expansions, and heat capacities of
neighboring phases as compression advances. Such shifts,
on occasion, can result from gradual promotion of an
electron from its normal orbital to one of higher energy
as in the curvature of the fusion curves of cerium and
caesium. Quantitatively, the curvature may be expressed
by differentiating the slope with respect to pressure:

$$\frac{d^2 T}{dp^2} = \frac{1}{\Delta V} \cdot \frac{dT}{dp} \left\{ \frac{\partial \Delta V}{(\partial p)_T} + 2\frac{dT}{dp} \left(\frac{\partial \Delta V}{\partial T}\right)_p - \left(\frac{dT}{dp}\right)^2 \frac{\Delta Cp}{T} \right\}$$

The equation illustrates how changes in compressibility,
thermal expansion, and heat capacity affect the curvature.

It is clear, therefore, that pressure always
favors the stability of the more dense phase. More often
than not, the denser phase also has the lower entropy,
but there are several exceptions as in the case of water-ice,
liquid and solid germanium, α-γ iron, etc. For these
substances the slopes of the phase boundary lines, dT/dp,
are negative. There are a few substances for which the
thermodynamic properties of adjoining phases are known and
and the initial directions, dT/dp, of their phase boundary

lines can be calculated, even extrapolated to several tens
of kilobars pressure, with fair reliability. The diamond-
graphite equilibrium to 40 kbars, 1200° K (Rossini and
Jessup, 1938) is a classic example of an effective calcula-
tion and extrapolation.

From the viewpoint of the low-pressure phase alone,
it is impossible to predict the occurrence or nature of a
new high-pressure structure (except by comparing with simi-
lar materials as noted below) and to forecast the direction
of the equilibrium line separating new and old phases.
Molecular orbital theory has not yet developed the ability
to decide how the bonding electron orbitals will rearrange
their directions and spacings or how they will redistribute
their energies. Thus, we discover phase boundary lines in
p and T space running every which way without prior notice.

The surprising effects induced by pressure can
be illustrated by the high-pressure properties of cesium
studied by Jayaraman et al.(1967b). This metal exhibits
several solid phases and a dimpled inverted V melting
curve (Fig. 12).

I   = body centered cubic (bcc),

II = face centered cubic (fcc)

III = collapsed form of II but with 6S electron
        promoted to 5d with some collapse in
        volume.

In the upward sloping parts of the melting lines, the solid
density is greater than the liquid density; however, in the
downward sloping regions, their relative volumes are in
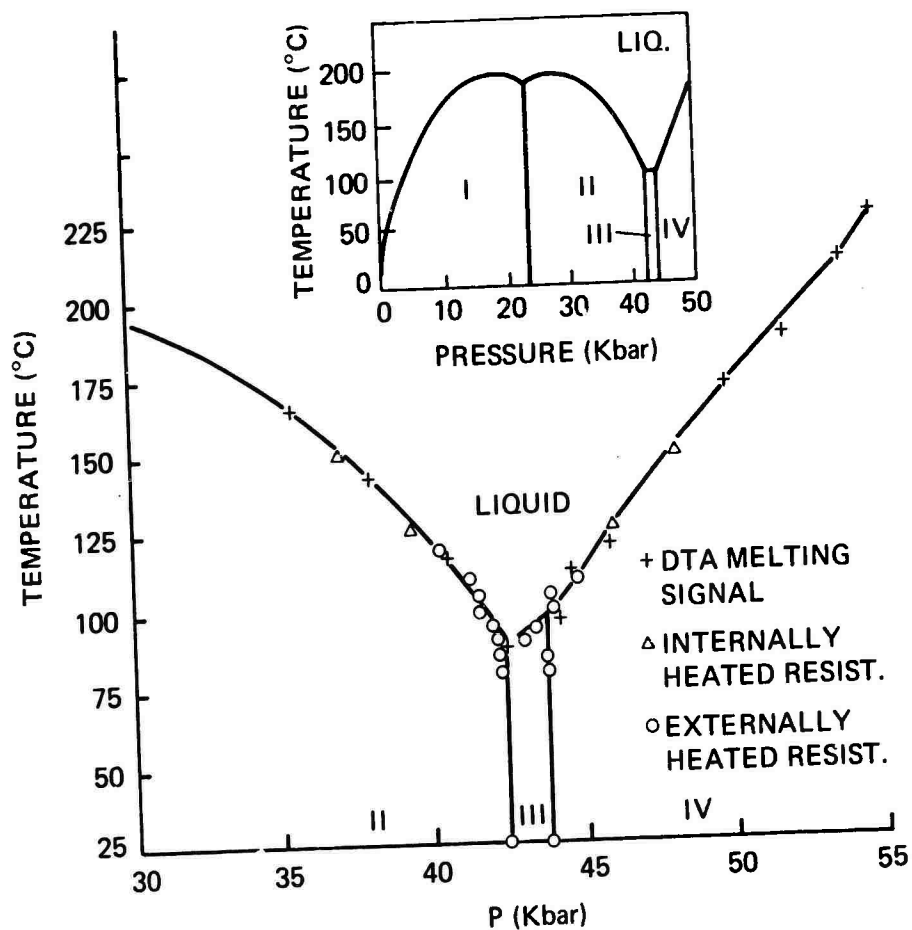reverse order.

FIGURE 12   Pressure-temperature stability diagram for cesium in the range 30-55 kbar and 25-225° C.   The insert shows the fusion curve and phase fields to 50 kbar, modified from Kennedy et al., Physical Review, 126, 1363, (1962).

Reproduced from: Phys. Rev., 126, 1363 (1962).

While there are many surprises of this type,
much help in guiding research to new discoveries has come
from comparing structures in isoelectronic series of
elements and compounds. These isoelectronic families
tend to form progressions of similar structures with change
of pressure and temperature. Thus, the group IV elements
are _isoelectronic_ with each other, differing in respect
to total quantum number, n, which runs from n = 2 to 6.
Group IV elements are likewise isoelectronic with III-V
and II-VI compounds, again with total quantum number
varying, n = 2 to 6. Cross combinations are permitted
with n differing for the two elements. However, differences
do creep in when the (Pauling's) electro-negativity dif-
ferences become so large that the normal covalent-type
bonding shifts gradually to ionic bonding with salt-like
structures replacing the graphite, diamond cubic, Wurtzite,
or metallic tin patterns of the group IV elements.

The group IV structure pattern with increasing
pressure is graphite (carbon and BN only), diamond cubic
(diam) or Wurtzite (Wtz), metallic tin, and fcc lead.
The heavier elements may exist stably in structures for
which the lighter elements require a great deal of pressure.
Thus, silicon and germanium are diamond cubic at zero
pressure, while carbon is as stable as diamond at room
temperature only for pressures exceeding 16 kbar. Silicon
and germanium are stable in the matallic white tin structure
at pressures exceeding 100 kbar, and revert back to meta-

stable intermediate structures when pressure is removed
(Bundy 1964). For the heavier elements in group IV to
attain the more open structures of the lighter elements,
negative pressures or reduced temperatures are required.
Only white tin exhibits a shift of this sort: from metallic
tin to the diamond cubic form when T is reduced.

Several isoelectronic families of elements and
compounds may be cited. For example, GeO_2, BPO_4, and BeF_2
are isoelectronic with SiO_2. Again, a structural pattern
has been recognized in which, with increasing pressure, we
find the sequence quartz $\rightarrow$ coesite $\rightarrow$ rutile $\rightarrow$ αPbO_2^* $\rightarrow$
possible fluorite or $CaCl_2$ structure[*]. Low-pressure SiO_2
has a succession of modifications with increasing temperature:
quartz, tridymite, cristobalite, and liquid. But BPO_4,
which occurs in cristobalite structure at zero pressure,
transforms to quartz at 40 kbar (Dachille and Roy, 1959).
Again, the heavier members have served as prototypes to
the high pressure modifications of the lighter members.

This characteristic relation between the high-
pressure forms of the light members in an isoelectronic
series vis-a-vis the low-pressure forms of the heavier
members was extensively exploited by Ringwood and others.
(Ringwood, 1969, and Akimoto et al., 1968 and 1971) to
explore inaccessible high-pressure phase transformations of

---

[*]Nagel and O'Keefe (1971) claim that in TiO_2 and the
difluorides, these are probably not thermodynamically
stable phases.

the pyroxenes in the deep mantle by studies on various
heavier isoelectronic analogues, especially the metal-
germanates.

The most important technological outgrowth of
reasoning from analogues was the discovery of cubic BN
by Wentorf (1957). This material was formed from the low-
pressure graphitic structure at pressures and temperatures
approaching those needed for diamond growth. Cubic BN is
technologically important because it is next in hardness to
diamond but chemically different so that it supplements
diamond in many industrial applications. Like diamond,
two modifications are known: zinc blende (zb) and wtz
corresponding to cubic and hexagonal or wtz diamond
(Hanneman, Strong, and Bundy, 1967). These two modifica-
tions seem to differ little in entropy, density, and other
physical properties.

Perhaps other technologically important materials
will be uncovered with similar reasoning. Very likely,
the new materials, with far-out properties, will be found
among the lighter elements of the periodic table. In order
that they may persist at zero pressure in their high-pres-
sure modifications, like diamond and cubic BN, they may
have to be formed at high temperatures. This will be
explained below under general rules and limitations.

a.   Certain guide lines for directing high-pressure
research towards specific goals are described above.
The following list of limitations, trends, and helpful
hints may be useful to the high-pressure researcher:

(1)   Solid→solid phase transformations tend to
spread themselves over a pressure range instead
of appearing sharply at the phase boundary line.
This is especially true for solids at tempera-
tures well below their melting points. Some
over-pressure may be required to form nuclei
of the new phase which must then grow. The
growth advance can be hampered by intergrain
boundaries and impurities or by loss of driving
pressure in material adjacent to growing nuclei.
The denser transformed material creates a
pocket of reduced pressure which may be bridged
over by the surrounding material. Finally,
the pressure apparatus usually has poor follow-
through characteristics so that the volume
shrinkage in the sample is not compensated by
piston travel. These are the sources of uncertain-
ty in recorded solid-solid phase boundary lines
which should be viewed as approximations.

A few solid-solid transformations can
be accelerated by additions of a solvent or
liquid catalyst to permit freer movement of
transforming atoms or molecules. Small amounts
of water are very effective in oxide and sili-
cate systems; molten metals are effective in the
carbon systems. But, the solvent introduces
a second component which can interact with
the solid to produce binary phases other than
those desired (Wentorf, 1966, and Strong and

Hanneman, 1967).

(2) In transforming to denser states, most
substances become more closely packed in the
sense that the coordination between constituent
atoms increases. The density of packing sequence
in many elements in terms of structure is simple
cubic (sc)→body centered cubic (bcc)→hexagonal
close packed (hcp)→face centered cubic (fcc).
Naturally, there are some exceptions wherein the
bcc structure is more dense than fcc or hcp
due to distortions of electron distributions,
as in Yb, Sr, Zr, Ti, and Te.

In groups IV, III-V, II-VI, the
succession of transformations, coordination
numbers, and properties are: (1) graphite,
coordination 3, light elements only, semiconduc-
ting in C-direction, metallic conducting in a-
direction (carbon only); (2) diamond cubic (diam),
zinc blende (zb), or wurtzite (wtz), coordination
4, semi-conducting; (3) metallic white tin,
coordination 4 and 2, metallic conducting;
(4) lead, fcc, metallic. The structures diam,
zb, and wtz differ little from each other in
density or entropy but have different stacking
orders.

The elements in group IV have pure
covalent bonding in the diam structure, but in
the III-V and II-VI compounds (zb or wtz),
the bonding is partly covalent, partly ionic.

In the heavier II-VI compounds, covalent bonding
gives way to predominantly ionic bonding so that
in place of the metallic tin structures, the
sodium chloride (B1) structure, coordination 6,
is found. When sufficiently compressed, B1
transforms to B2, cesium chloride structure,
coordination eight.

In the SiO_2 series, and similarly in
its analogues, the coordination of Si with
oxygen increases in the sequence quartz, coesite,
4-fold coordination; rutile, α -PbO_2 structure,
6 fold coordination; possibly the fluorite struc-
ture at still higher pressures, 8 fold coordina-
tion.

(3) Very few high-pressure phases persist for long
after the pressure is removed. Sometimes, as in
the case of germanium, (Bundy, and Kasper and
Richards, 1964) the high-pressure phase reverses
to a metastable intermediate phase with the same
coordination but higher density than the diam form.
this inability to return alive most high-pressure
forms deprives the researcher of the opportunity
to more closely examine and use the interesting
properties that might otherwise be available.

The exceptions to the usual behavior
are found mostly in those forms that require both
high pressure and high temperature to run the
transformations. This implies that a substantial
activation energy barrier normally retards the

rate of the transformation in either direction.
Diamond and cubic BN, both formed at high temperature,
are the best examples of persistent metastable forms
at zero pressure. Coesite and stishovite (rutile
structure) high-pressure high-temperature modifica-
tions of SiO_2 also persist at zero pressure. Both
of these latter minerals were found in the Canyon
Diablo Meteor Crater where they were formed by an
impact which occurred at least 20,000 years ago.

There are a few instances in which stubborn-
type transformations will run at moderate temperatures
when the pressure is greatly in excess of equilibrium.
The formation of cubic diamond, hexagonal diamond,
and both zb and wtz BN are examples in which
pressurizing to from 0.3 to 1.5 megabar causes
the transformations to run in microseconds at tem-
peratures $\lesssim 1,000°$ C. In these examples, the re-
action paths are altered by the severe compression
so that the activation energy barrier is greatly
reduced.

Actually, these ultra-fast reactions may
represent an example of Libby's (1962) proposal that
materials compressed into the metallic state might
transform into a non-metallic state (stable or meta-
stable) upon release of pressure. The metallic
bond's non-directional character, would offer no
hindrance to directional bond formation. Dynamic
shock compression brings carbon very close to the
metastable metallic liquid state of graphite where

bond directionality may be largely erased permitting the rapid transformation to diamond.

(4)   Many elements melt from the bcc structure which tends to be the predominant high-temperature form.   The bcc phase of iron at just below the melting point persists to ~ 52 kbar, 1,718° C where there is a triple point between liq, bcc, and fcc iron (Strong, unpublished data 1972).   Above the triple point, iron melts from a fcc solid.   Copper, silver, and gold are other exceptions which are fcc at the melting point.

(5)   So far, there is no evidence for a solid-liquid critical point comparable to a liquid-gas critical point, in any substance.   However, at extremely high pressures, it is expected that the difference between solid and liquid will gradually fade away as the increasing compression permits a closer approach to the Thomas-Fermi state of ions embedded in a sea of electrons.

It is fortunate that not all elements undergo high-pressure phase transformations within the explored pressure ranges.   Some stable materials are needed for apparatus, lead wires, thermocouples, capsules, heaters, probes, etc., in high-pressure experimentation.   The important stable elements are: (1) the "hard" metals V, Nb, Ta, Cr, Mo, W; (2) the group IB metals, Cu, Ag, Au; (3) the platinum-group metals Rh, Ir, Pd, Ni, Pt; and (4) the group III metals Al and In. Aluminum has been subjected to megabar pressures with no sign of solid-solid phase transformation. Amongst the high melting-point hard metals, only Ta and Mo have had their high-pressure

fusion curves determined: Ta from 2996° C at zero pressure to 3500° C at 60 kbar (Fateeva and Vereschagin, 1971), and Mo. No change in the solid structure of Ta or Mo was reported in these experiments.

In recent years, interest has been running high in binary and ternary oxides, chalcogenides, fluorides and chlorides, etc. Among these compounds, a seemingly endless variety of combinations are emerging, many with interesting properties, including magnetic, ferro-electric, optical, tunnel lattice passages (possible solid electrolyte), band gap materials, etc.

Formation of these interesting materials sometimes requires pressure at high temperature, which helps to insure their stable metastability at room conditions. The pressures required are generally less than 60 kbar.

Some of the persons who have published in this area are: Singh, Jayaraman, Chatterjee (1971); Yu and Geliesse (1971); Rooymans (1965, 1969); Goodenough, Kafalas, Longe (1972); Goodenough (1972); and Previtt and Shannon (1969).

b. Anticipating new forms of matter bears a likeness to weather forecasting; one relies largely on recognizing patterns. The thermodynamic approach is helpless without data on properties of both phases. The molecular orbital approach is also of little use because the structures are far too complex for mastery. But patterns of behavior there are; and as we have seen, these have been useful. Meanwhile, gradual progress is being made in analyzing structures, and measuring or calculating expansion and compressibilities of high-pressure phases (for example, the works of Decker, 1971;

Jamieson, 1960, 1963, 1964; Kasper, 1969; and Swenson, 1971,
have contributed substantially in this area).

Plendl and Gielisse (1969) have proposed an interest-
ing method for anticipating structural changes associated with
either a temperature or a pressure increase. They noted that
the compressibility of many substances followed a linear rela-
tionship with $\rho \frac{.ZE_B}{r_o^3}$ in which r_o^3 is proportional to volume/atom in
the crystal, Z the valence, E_B an energy constant identical with
the stationary energy of an electron in the L-orbital correspond-
ing to total quantum number n = 2 in the Bohr energy term,
$E_B = \frac{2\pi^2 e^4 m_o}{n^2 h^2} = 5.448 \times 10^{-12}$ erg. ρ is the ratio of coordination
numbers in the modified state vs the "base state." For many
materials $\rho = 1$ and a plot of compressibility vs $\frac{ZE_B}{r_o^3}$ yields a
straight line. For $\rho > 1$, the material is said to be in an
"elevated" state and may be brought back to the base state by
a reduction of pressure or increase of temperature. For $\rho < 1$,
the material is in a "reduced" state and may be transformed to
the base state by means of increased pressure or reduction of
temperature. Their results were applicable to some 90 binary,
ternary, or quarternary solids having 25 different structural
types and valences from one through six.

In a somewhat related development, Previtt and
Shannon (1969) have shown how effective ionic cation radii
in oxide and fluoride crystal structures are related to the
volume of the unit cell. They showed that in isotypic series
of rutile structures or jadeite structures, the unit cell
volume is a linear function of the cation radius cubed. For
example, in rutile, RO_2, structures where R = Si, Ge, Cr,
Ti, Pt, Mo, Sn, Pb, etc., unit cell volume is a linear function
of r^3 for cation R radii. It is particularly interesting

that in the case of R = Si, SiO_2 is in the high-pressure stishovite form. This fact suggests that their empirical rule has predictive capability for new crystal compositions in various complex oxide structures that may be derived by using pressure to adapt either smaller cations (i.e., Si in rutile) or larger cations (i.e., In^{3+}, Tl^{3+} in corundum) into structures already well known as low-pressure forms. In this way, the variety of physical properties available may be greatly extended. Many oxide and di-fluride structures formed at high pressure and temperature are recoverable at zero pressure.

Melting behavior under pressure continues to receive considerable speculative attention. During the past several years, a number of melting-point extrema have been observed, such as the melting-point minimum for cerium and the maxima among the alkali metals. It has been suggested by Yoshida and Okamoto (1971) that with continued compression, the potential energy of crystal-bound atoms can increase faster than those in the liquid state until the difference between the two energies becomes less than kT, when the crystal will melt. They have had some success applying their calculations to cesium and rubidium melting temperature maxima. The occurrence of maxima melting curves have been proposed as "normal" melting behavior by Kawai and Inokuti (1968). Maxima have not been seen in the more incompressible elements.

Looking far into the future, we may see more electronic transitions of the type already demonstrated in both cesium and cerium. Izmailov and Shuliman (1966) have suggested that under compression, states with higher orbital quantum numbers tend to become filled as compared to free atoms or low pressures where these states remain unfilled. Hence, if all atoms were sufficiently compressed, a new

periodic table of the elements could be generated. The
pressures needed may be in the range of 3 to 40 mbars for
many elements.

4. CHEMICAL SYNTHESIS

Sometimes high pressure is useful in the simple role
of mechanical confinement, i.e., keeping volatile substances
imprisoned while they participate in high-temperature reactions.
Thus, Munson (1968) synthesized IrS_2 and $NiAs_2$ in the pyrite
structure and Rooymans (1967) and others describe the synthesis
of many spinels and chalcogenides. CrO_2 and $PbCrO_3$ were
synthesized at 60 kbars, 1500° C by Devries (1967) and Devries
and Roth (1968). Pressure confined the high oxygen or sulphur
vapor pressures during the reactions. Forming alloys or inter-
metallic compounds between metals of widely separated melting
points can likewise be aided by this technique, for example,
Ti-Mg alloys (Oriani and Strong, 1966). In one of the very
early high-pressure reactions, Bridgman (1964) polymerized
CS_2 at ~30 kbars, 200° C.

The latter example illustrates the far reaching
effects of high pressure on organic reactions, that may be
radically altered in character, rate, or both. Thus the
decomposition of acetone may be prevented by pressure and
its polymerization greatly accelerated at 350° C, 40 kbars
(Bengelsdorf, private communication, 1958). Bengelsdorf
(1958) reported the rapid trimerization of aromatic nitriles
to triazines at 30 to 50 kbars. In like manner, the dinitriles
such as succinonitrile and malononitrile are rapidly poly-
merized in the solid state at 450° C, 50 kbars (Hara, 1970).

Pressure does not always aid chemical reactions con-
structively. In an opposite role, Bengelsdorf (private
communication, 1959), found that when compressed at 35 kbars,
30° C, bicycloheptadiene was completely unstable and carbonized
in 45 minutes.

In thinking about chemical reactions, one must con-
sider the activated state of the reacting molecules in which
the Gibb's free energy is higher than that of the reactants
or products. Generally, the volume of the activated state is
different from that of the reactants and products. Activation
volumes commonly lie in the range $\pm$ 25 cm^3/mol for organic
reactions. If the activation volume change is $\Delta V^* = \pm$ 10 cm^3/mol,
a pressure of 40 kbars will contribute 10 kilo calories to the
free energy of the activated state; an amount approaching the
chemical reaction energy. Thus, one can easily see that
pressure will greatly affect the reaction rate through the
term $p\Delta V$. For negative ΔV values, the reaction will be speeded
up -- possibly beyond the need for catalysts if the final pro-
duct is more dense than the reactants. For positive ΔV, the
reaction may not occur at all or may seek some other reaction
path and product with more favorable ΔV's.

For more complete discussions of high-pressure
effects in organic chemistry see Weale's (1967) review of
basic principles, techniques, and results of studies in 1- to
15-kbar range; Kohnst's (1970) discussion of kinetic effects
of pressure; Gay's (1971) review of pressure dependence of
activation volume; and R. E. Hanneman's "Effect of Pressure
on Phase Transformation Rates," (1969).

5. OVERSEAS ACTIVITIES IN HIGH PRESSURE

The open literature, a few meeting summaries, and personal observations from some of General Electric Company's representatives in Europe and in Japan provide impressions about activities in high-pressure technology on the foreign scene. It seems clear that there are very many people engaged in this type of research and, in Japan at least, the number of people so engaged is still increasing. The research in which they are involved spans the same broad spectrum as U. S. work. In addition, some of the Europeans seem to have more background in the areas of supercritical fluids and mechanical extrusion than do Americans. In other areas, high-pressure work is still a novelty and researchers are happily engaged in redesigning and calibrating high-pressure gear. In this summary, Russia, Europe, and Japan are considered separately.

a. Russia: Russia has a large institute, located near Moscow and directed by L. F. Vereschagin, for high-pressure research. The Russians publish many papers on the subjects of apparatus, superconductivity, and phase transformations in mineralogic substances, diamond, and cubic BN. Most of their publications relate to the latter two topics and many of these are only one or two pages long, revealing little essential detail.

The Russians often refer to their 50,000-ton press and associate this press with their plans for generating one megabar pressures. However, no description of the apparatus that is to support this pressure has been seen, and no evidence has been offered for having attained pressures near one megabar.

Some of their work on superconducting materials
and geologic minerals has been a first-rate pioneering
effort. Their publications relating to diamond and cubic
BN contain nothing significantly new or different from
the U. S. contributions on these topics. A good portion
of their diamond work is considerably behind U. S. work,
while their cubic BN work runs about even in recent years.

The Russians have succeeded in growing diamond
whiskers at low pressure and have made some progress
in obtaining n-type diamond by ion implantation. The
diamond whiskers, according to first-hand reports from
their makers, have no technological value. The n-type diamond
development could be useful because only p-type can be
formed in growth.

b. Europe: There are many high-pressure research
groups scattered throughout Western Europe, probably
none of them as large individually as the Institute
in Moscow. All of these laboratories are turning out
a great deal of work on various kinds of electrical
measurements under pressure, phase transformations and
structure work, particularly with chalocogens and oxides
of transition metals, and geophysical studies. An
interesting type of study on supercritical liquids has
been going on for many years at Karlsruhe under E. U.
Franck. Ion mobilities, etc., are being measured
under pressures ranging from 10 to 100 kbars. Another
pioneering effort on metal extrusion and mechanical
properties has been in progress for many years under
H. Ll. D. Pugh in Scotland. Other laboratories seem to be

studying the types of things that have been done in the
U. S. -- phase transformations, structures, electrical,
magnetic, superconduction, and Hall-effect properties.
A good deal of effort has been expended, probably need-
lessly, redesigning apparatus and elaborating on cali-
bration. On the whole, European work seems to be of
good quality.

c. Japan: The Japanese are very ambitious and this is
reflected in the variety and quality of their work.
Their high-pressure activities are widely scattered in
Japanese industries and universities and are conducted
individually or in small groups. The range of work
includes theory, geophysical research, neutron diffraction,
radioactive decay under pressure, organic reactions--
polymerization, diamond and cubic BN, phase transforma-
tions, structure and electrical conductivity studies
down to liquid helium temperatures, and melting phenomena.

While their diamond and cubic BN work is virtually
a duplication of U. S. work, in other areas they seem
to be opening new ground and may have improved apparatus
with greater than 300-kbar capability.

The Japanese have done well and are expanding their
efforts.

d. Summary: The products of all the thousands of high-
pressure experiments conducted all over the world repre-
sent great strides in understanding matter, structures,
and geophysical problems of the deep mantle but have
resulted in only two technological products, diamond
and cubic BN.

The small, independent laboratories of Europe and Japan have been most effective in producing a large variety of innovative scientific and technological results. The concentration of effort into a single large institute has been effective in Russia for focusing on a few restricted areas such as diamond and cubic BN and for advancing their own technological skill with these materials.

6. RESEARCH RECOMMENDATIONS

In conclusion, it seems desirable to comment on a number of problem areas of relatively direct interest to the DoD.

a. Development of 1-Megabar Pressure Capability:

This problem was discussed in the apparatus summary. It is suggested that an apparatus project patterned after Kawai's spherical design may be effective. Tungsten carbide anvils seem to have given Kawai good results; however, some of the new tungsten-carbide-backed diamond compact materials might be useful as well for the anvil tips in the spherical design.

As a first step, 400- to 500-kbar pressure capability would be quite rewarding, but it is difficult to know when one of these higher goals has been achieved. One suggestion for a possible high-pressure reference point would be the direct transformation at room temperature cf graphite to diamond, which should run at 400 to 450 kbar (Bundy, 1962). This transformation at room temperature has never been reported.

b. Material and Property Investigations: An example
of possible technologically important products of high-
pressure research are the alkali antimonates described
by Goodenough. These compounds have tunneled structures
that may be useful in energy storage as solid-state
electrolytes in a battery. Inquiry into this develop-
ment might lead to further useful research towards a
product.

Another example is laboratory-made gem-quality
diamonds with tailored properties. These have controllable
properties of high purity, thermal and electrical conductivity,
optical characteristics, abrasion resistance, and strength.

An analogous potential exists for unique electrical
and optical properties in cubic BN crystals as new high-
pressure growth methods now under development yield a
variety of crystals. Fundamental property studies of
such crystals will be required along with more practical
problems, such as metal to boron nitride bonding with
acceptable electrical resistance for device considerations.

These three examples: (1) tunnel structured dielec-
trics, (2) diamond with tailored properties, and (3)
cubic boron nitride with tailored properties offer poten-
tial for unique physical properties over existing materials
for helping to meet DoD needs, especially in device tech-
nology. One possibility is the use of high-purity lab-
oratory diamonds in electronic devices as either: (1)
"heat sinks," or (2) as Schottky-barrier diodes. Their
suitability as heat sinks has already been proven. Their
potential for diodes needs more study. The diode applica-
tion is attractive because of the self-cooling property

of diamond not found in any other existing diode material. There is consequently the possibility of attaining higher power levels in diamond than is presently done in other diode materials.

The identification of a suitable material for a specific application would have to be followed by practical engineering work on crystal growing, purification, fabrication, device development and economic studies.

While many new forms of matter have been identified in high-pressure research, there are surely many more hidden from view that have some small chance of being technologically important. Consequently, the continuation at moderate funding of systematic materials research, guided closely by theory, to be conducted at several small laboratories will serve the human need-to-know. Also, it is the method by which progress in high-pressure research in other countries may be followed.

<u>c</u>. <u>Superhard Bearing and Cutting Tool Materials:</u>

These items are considered together because both are likely to have the same material-problem solution.

The question of whether there are better superhard materials has been reviewed by Prendl (1961), Prendl and Gielisse (1962), and by industry. There is a close correlation between crystal cohesive-energy density and abrasive hardness of materials (see Fig. 13). Diamond remains unexcelled with a cohesive-energy density of 1400 kcal/cm^3. Abrasion resistance, compressive strength, and friability of synthesized diamond and cubic
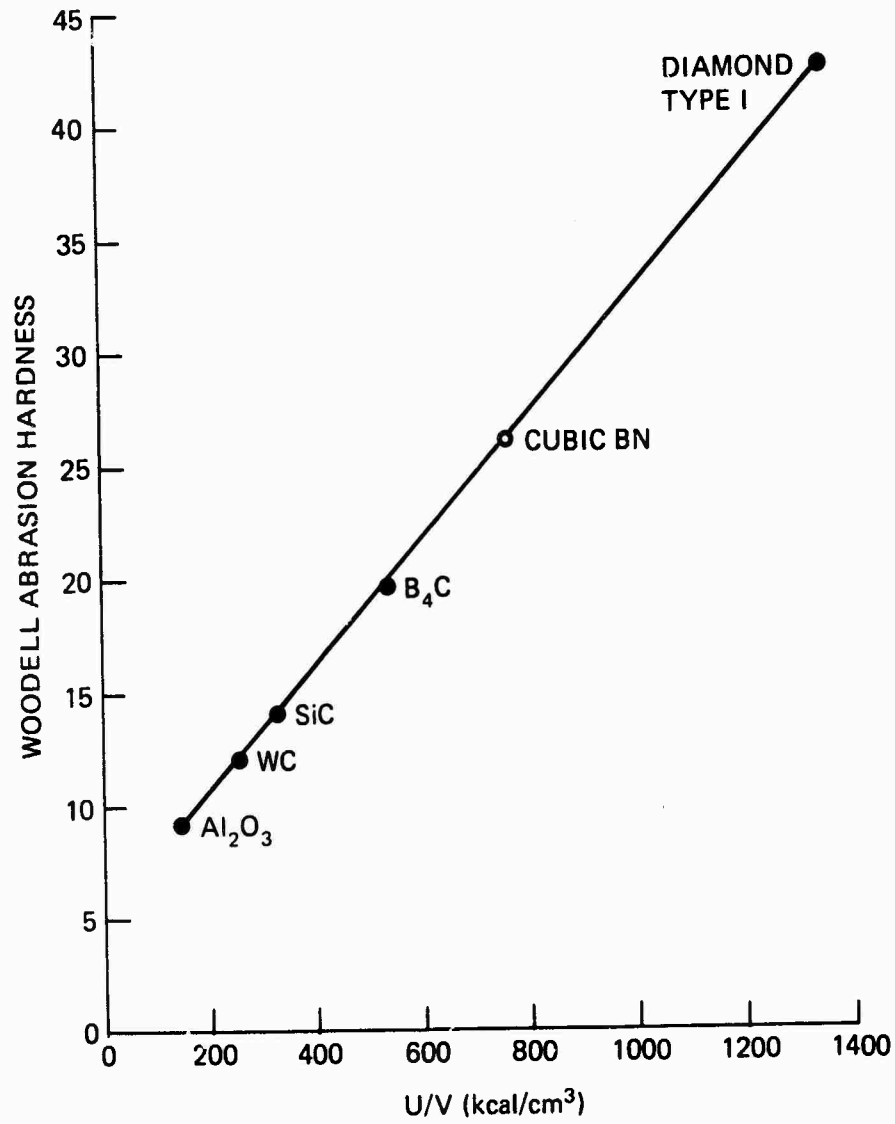
Fig. 13   Relation between density and hardness.

BN crystals can be altered considerably by impurity and process control.

It has been possible to enhance further the utility and application of diamond and cubic BN by forming densely sintered compacts of small crystals of these materials. In some cases, these compacts are bonded to a high-strength tungsten carbide substrate. The diamond and cubic BN crystals may be work-hardened somewhat in the sintering process and the random orientation of the crystallites block cleavage crack propagation. These very recent developments, proposed earlier as a need by DoD, have now gone through the laboratory development stage as well as extensive engineering development, practical trials in real production settings, and cost effectiveness and marketing studies. These unique new products represent a breakthrough in cutting tool technology that should have important impact in machining a wide range of ceramic and composite materials as well as difficult-to-machine alloys. Detailed studies of the mechanisms of tool wear and failure and a re-definition of machinability criteria and parameters will be required for this new class of tools to accelerate their use broadly. The preliminary indications are that benefits can include much higher material removal rates, improved surface integrity, and greatly extended tool life. Limited applications to date of DoD interest have included machining of missile nose cone materials, submarine bearing seals, ceramics, composites, and super-alloys. In addition, superhard compact materials are being adapted for bearing materials, wire drawing dies, and other applications.

Among the problems listed by DoD were those of shaping boron nitride and sapphire. These are presently most easily handled with diamond tools, including diamond-studded saws, grinding wheels, and single point diamond tools. However, abrasive and cutting properties vary between diamonds. For single-crystal diamond tools, low-nitrogen type II diamonds may be more durable than the "run of the mine" nitrogen-containing diamond. In some problems of this type, it is quite possible that much help can be gained at no cost to DoD by consulting people with wide experience in industrial diamond applications.

The cutting tool business is a very active and highly competitive one. The motivation for new developments within the industry is intense so that there are frequent significant improvements being made. The DoD is sure to benefit by the efforts being made in the private sector on cutting tool problems and will be able to accelerate the adoption of these developments through substantial support in new machinability studies and fundamental analyses of machining processes involving new compacts of superhard materials. It is this limitation of machinability understanding that appears to be limiting the rate of adoption of these new tools in certain key areas at this time.

It is intriguing to consider possible new hard structures formed from one or more combinations selected from the elements C, B, N, Be, Si, Al, and P. While B and N substitute easily in diamond, it has not yet been possible to form a hybrid crystal of NBC or to form a two-phase system of BN in diamond, or inversely, diamond in cubic BN. The possibilities among these seven elements

have not been exhausted, but there are no uniquely
promising leads at present. If it were possible to
obtain the metallic states of SiC, BN, or diamond,
it would be interesting to try again to form hybrid,
or two-phase, crystal systems. Probably pressures in
the 60- to 150-kbar range at high temperatures would
be needed to induce new reactions of interest.

It is not likely that any of these would be
harder than diamond, but they might have chemical
characteristics that qualify them for cutting work
not fully suited to diamond or BN.

A program of study of this type should probably
have only fairly modest support at this stage.

d. Metallic Hydrogen: It has been suggested that
metallic hydrogen would be a high-temperature super-
conductor and therefore a worthy goal for high-pressure
research but all speculation relating to metallic
hydrogen is very "iffy."

The pressure needed to induce the metallic state
is presently estimated to be between 1.7 and 5.6 mega-
bars; however, even this range is uncertain. The
corresponding density was estimated at 1.6 gm/cm^3.
Comparing this with its S T P density, 0.00089 gm/cm^3,
it would seem fairly unlikely that the metastable phase
of this material could be frozen-in at atmospheric
pressure.

Another unsolved problem is that of introducing the
hydrogen into the high-pressure cell.

For the present, the pressure and the handling techniques are not available to start this project. Two parallel approaches appear to be justified at this stage regarding metallic hydrogen. First, a more adequate theoretical study of the metallic hydrogen transition should be considered now that includes the more advanced molecular orbital approaches successfully being adopted recently to other solid-state materials. Such treatments could probably be adopted to the metallic ammonia transition. Secondly, it is suggested that with the possible extension of the pressure range to 500 kbars, the metallic ammonia problem might be a good place to start experimentally. As pressure equipment and capability evolve, metallic BN and SiC might occur and finally, metallic carbon and metallic hydrogen might be obtained. Any experimental program on metallic hydrogen should await a more thorough theoretical evaluation of the properties and transition conditions.

e. Superhard High-Density Materials for Penetration:

There does not seem to be any better generally available material than tungsten carbide for penetration. The properties of tungsten carbide have recently been improved by a hot pressure sintering method.

Any new, more dense, hard material generated by high pressure is likely to be too expensive for large volume application to projectiles. Therefore, this is not a promising project for high-pressure research and does not justify significant support.

f. <u>Summary</u>: Our consideration of the opportunities for the application of high-pressure research to technological materials and properties advances of relevance to DoD shows substantial promise for only selected areas.

This is partly the case because of the inherently small volumes that are achievable at very-high-pressure conditions, partly because of the very high intrinsic costs of high-pressure process, and partly because of the difficulty to "freeze-in" certain phases or properties achieved upon return to atmospheric pressure. The most promising opportunities appear to lie in: (1) the processing and use of very high unit value high-pressure materials such as diamond or cubic BN for tailored applications ranging from devices to cutting tools, and (2) unique high-pressure processing of "low pressure materials" (such as extrusion, drawing, and deformation of metals, and sintering of ceramics). Significant contributions to other carefully selected technological and scientific problems will be made by both theoretical and experimental studies using pressure as a key variable, but these should be carried out on a more modest basis.

ACKNOWLEDGEMENT

BIBLIOGRAPHY

S. Akimoto and Y. Sato, Phys. Earth Planet Interiors, 1, 498 (1968).

I. S. Bengelsdorf, J. Am. Chem. Soc., 80, 1442 (1958).

P. W. Bridgman, "Collected Experimental Papers," Harvard University Press (1964).

F. P. Bundy, J. Appl. Physics, 32, 483 (1961); Science, 137, 1057(1962); J. of Chem. Physics, 41, 3809 (1964).

F. Dachille and R. Roy, Z. Krist, 111, 451 (1959).

D. L. Decker, J. Appl. Phys., 42, 3239 (1971).

R. C. De Vries, Mater. Res. Bull, 2, 999 (1967; and W. L. Roth, J. of Am. Ceram. Soc., 51, 72 (1968).

N. S. Fateeva and L. F. Vereschagin, JETP Lett., 14, 1953 (1971).

I. C. Getting and G. C. Kennedy, J. Appl. Physics, 41, 4552 (1970).

J. B. Goodenough, "High Pressure Technology and Magnetism." (Appendix J)

J. B. Goodenough, J. A. Kafalas, and J. M. Longo, High Pressure Synthesis in "Preparative Methods in Solid State Chemistry," P. Hagenmuller, Ed., Academic Press,(1972).

R. E. Hanneman and H. M. Strong, J. of Appl. Physics, 36 523 (1965).

R. E. Hanneman, "Reactivity of Solids," J. W. Mitchell, et al., Ed., Wiley-Interscience (1969).

R. E. Hanneman, H. M. Strong, and F. P. Bundy, Science, 155, 995 (1967).

K. Hara, Rev. Phys. Chem. Jap., 40, 73 (1971).

S. V. Izmailov and G. A. Shulman, Soviet Physics-Tech.Physics, 10, 1455 (1966).

J. C. Jamieson, Fourth Annual ONR Report, p7 (1960);
Science, 193, 762 (1963); Science, 145, 572 (1964).

A. Jayaraman, R. C. Newton and J. M. McDonough, Phys. Rev.,
159, 527 (1967b).

J. S. Kasper and H. Brandhorst, J. Chem. Phys., 41, 3768 (1965).

J. S. Kasper and S. M. Richards, Acta Cryst., 17, 752 (1964).

J. S. Kasper, Trans. Amer. Crystal. Assoc., 5, 1 (1969);
Amer. Cryst. Assoc., Polycrystal Book Service, Pittsburgh,
Pa., 15238.

N. Kawai and Y. Inokuti, Jap. J. Appl. Phys., 7, 989 (1968);
Jap. J. Appl. Phys., 9, 31 (1970).

W. Klement, Jr. and R. Jayaraman, "Progress in Solid State
Chemistry," Vol. 3, H. Reiss, Ed., Pergamon Press (1967).

G. Kohnstam, Prog. in Reaction Kinetics, 5, 337 (1970).

W. F. Libby, Proc. Nat. Acad. Sciences, 48, 1475 (1962).

R. A. Munson, Inorg. Chem., 7, 389 (1968).

L. Nagel and M. O'Keefe, Mat. Res. Bull., 6, 1317 (1971).

R. A. Oriani and H. M. Strong, Trans. Met. Soc., AIME, 236,
1508 (1966).

J. N. Plendl and P. J. M. Gielisse, Phys. Status Sol.,
35, k151 (1969).

C. T. Prewitt and R. D. Shannon, Trans. Amer. Cryst. Assoc.,
5, 51 (1969).

A. E. Ringwood, Earth and Planetary Science Letters, 5,
401 (1969).

C. J. M. Rooymans, "High Pressure Studies of Oxides and
Chalcogenides," Ph.D. Thesis, Amsterdam University,
Netherlands, Solid State Commun. 3, 421 (1965); also,
Philips Res. Suppl., 5, Eindoven, Netherlands (1968).

C. J. M. Rooymans, "Review on Chalcogenides - Atomic Radii," Adv. High Pressure Research, 2, 1; R. S. Bradley, Ed., Academic Press, London (1969).

F. D. Rossini and R. S. Jessup, Nat. Bur. Stds. J. Res., 21, 491 (1938).

A. K. Singh, A. Jayaraman and A. Chatterjee, Solid State Com., 9, 1459, Pergamon Press (1971).

H. M. Strong, Modern Very High Pressure Techniques, R. H. Wentorf, Jr., Ed., Butterworth (1962).

H. M. Strong and R. E. Hanneman, J. of Chem. Phys., 46, 3668 (1967).

C. A. Swenson, "Phys. & Chem. of Solids under High Pressure," Vol. 1, (1970)

Y. Syono, Sakimoto and Y. Matsui, J. Solid State Chem., 3, 369 (1971).

L. F. Vereschagin, A. A. Semerchan, V. P. Modenov, T. T. Bacharova, M. E. Dmitriev, Doki. Akad. Navk. SSSR, 195, 137,593-4 (1970).

R. H. Wentorf, Jr., "A Treatise on Physical Chemistry," W. Jost and H. Eyring, Eds., J. Chem. Physics, 26, 956 (1957).

R. H. Wentorf, Jr., Ber. Bunsenges Phys. Chem., 70, 975 (1966).

K. E. Weale, "Chemical Reactions at High Pressures, E.& F.N. Spon, London (1967).

E. Wigner and H. B. Huntington, J. Chem. Physics, 3, 764 (1935).

T. Yoshida and H. Okamoto, Prog. in Theor. Phys., 45, 663 (1971).

W. C. Yu and P. J. Gielisse, Mat. Res. Bull., 6, 621 Pergamon Press (1971).

APPENDIX E
CALIBRATION OF THE SUPPORTED TAPER
CELL FOR ELECTRICAL WORK

by H. G. Drickamer
University of Illinois, Urbana, Illinois

In Appendix D Dr. Strong indicates the pressure
limitations on various types of equipment as seen by the
General Electric Company. It seems desirable to include a
note on the calibration of the tapered piston cell for elec-
trical work to permit people to judge the methods of calibra-
tion and the pressure limitations. It is important to note
that all the results discussed were obtained using tungsten
carbide pistons with 3% binder. The pistons were thoroughly
work-hardened and reground as described in the original
papers. Failure to work-harden provides a very severe
limitation on the pressure range.

In 1960 a high-pressure electrical resistance cell
was developed in the University of Illinois laboratory, [1]
utilizing the supported taper principle previously applied
to an optical apparatus.[2] The calibration of the electrical
cell was tenuous since it was based on some poorly located
phase transitions at low and moderate pressure plus a gross
extrapolation of Bridgman's electrical-resistance data for
platinum.[3] Since that time a number of transitions have
been located more accurately and x-ray diffraction techniques
utilizing the tapered piston cell[4] have become available.

A new calibration, based largely on x-ray diffrac-
tion work, is presented here. The piston diameter and

internal geometry of the x-ray call can be made identical to
the electrical cell (22 mm in diameter, 2 mm flat, 18° taper),
but the x-ray cell contains a layer of lithium hydride and
boron with platinum collimation in addition to pyrophyllite,
while the electrical cell contains only pyrophyllite. Never-
theless, this calibration represents a considerable advance
over the previous one. Many of the calibration data were
taken with Al or Ag powder, using the shock data of Rice et al.[5]
interpolated to room temperature.[6] The 111, 200, 220, and
311 lines were utilized. Above 250 to 300 kbars, the dishing
of the pistons made it impossible to obtain the 220 and 311
lines clearly. Data were also obtained for NaCl to over
200 kbars. Applying Decker's calculated p-v values for
NaCl,[7] the Al and Ag data were closely checked. MgO[8] also
gave consistent results to 300 kbars.

The calibration is established as follows: The
pressure is a linear function of applied force to 100 kbars
(and substantially linear to 130 kbars). For higher pressures
the change of pressure (from 100 kbars) vs fractional change
in applied pressure is shown in Table I. This was obtained
by taking the fractional change in pressure with the fraction-
al change in applied force from the x-ray data to 400 kbars
and extrapolating primarily by assuming the relative pressure
is a linear function of the logarithm of the relative
applied force at pressures above 400 kbars. (This condition
holds quite well in the range 300 to 400 kbars.) X-ray data
above 400 kbars are limited. There are a few x-ray data
(e.g., on the 111 and 200 lines of Ag, which extend to 475
kbars). X-ray data on CsCl[8] to 450 kbars fit very closely

the extrapolation of shock and other data by the Born-Mayer
or Mie-Grüneisen equation.

In Table II appear the old and new pressures
obtained from typical calibration curves for a number of
transitions. These are not presented as standards. The
CdS maximum has been reproduced in several laboratories.
By 450 to 460 kbars the resistance of CdS has dropped to
~60% of the maximum. By ~460 to 440 kbars the resistance in
ZnS has dropped by 20% from its maximum value at ~420 kbars.
Another possible point involves the rather distinct increase
in resistance for barium at ~420 kbars <u>and 77° K</u>. By 500
kbars it has increased about 70% from the value at the
shallow minimum near 400 kbars. This point is of use only
at 77° K. It is of interest to note that the transitions in
the low pressure region generally agree reasonably well with
recent values obtained in other laboratories.

REFERENCES

1. A. S. Balchan and H. G. Drickamer, <u>Rev. Sci. Instrum.</u>,
    32, 308 (1961).

2. R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer,
    <u>J. Opt. Soc. Amer.</u>, 47, 1015 (1957).

3. P. W. Bridgman, <u>Proc. Amer. Acad. Arts Sci.</u>, 81, 169
    (1952); <u>Proc. Amer. Acad. Arts Sci.</u>, 83, 1 (1954).

4. E. A. Perez-Albuerne, K. F. Forsgren, and H. G. Drickamer,
    <u>Rev. Sci. Instrum.</u>, 35, 29 (1964).

5. R. H. Rice, R. G. McQueen, and J. M. Walsh, <u>Solid State
    Phys.</u>, 6, 1 (1958).

6. H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A.
    Perez-Albuerne, <u>Solid State Phys.</u>, 19, 228 (1966).

7. D. L. Decker, J. Appl. Phys., 36, 157 (1965).

8. E. A. Perez-Albuerne and H. G. Drickamer, J. Chem Phys., 43, 1381 (1965).

TABLES

TABLE I. Electrical Cell Calibration. Pressure vs. Applied Pressure. (Related to pressure necessary for 100 kilobars.)

Pressure (in kilobars)	$P_{APP}/P_{100 \text{ kilobars}}$
100	1.00
130	1.32
150	1.60
200	2.50
250	3.80
300	5.60
350	8.20
400	12.00
450	16.70
500	24.00

TABLE II. Approximate Location of Transitions.

	Old	New
Bi	88	73–75
Fe	133	110–115
Ba	144	118–122
Eu	150–160	122–130
Pb	160	128–132
Rb	190	142–153
Cs[a] (max)	170–180	133–142
Ca[a] (max)	350–375	235–255
Rb[a] (max)	420–435	290–320
CdS[a] (max)	460	320–340
ZnS[a] (max)	550	410–420

[a]Maximum in resistance–pressure curve.

APPENDIX F

SOME KINETIC PROBLEMS IN
VERY HIGH-PRESSURE RESEARCH

by D. Turnbull

Harvard University, Cambridge, Mass.

The effects of pressure on kinetics of reactions and phase changes in condensed systems have been reviewed elsewhere.[1] In this appendix some high-pressure kinetic phenomena that are not well understood, in particular marked pressure enhancements of crystal growth rates in some systems, will be discussed. A satisfactory understanding of these effects would provide valuable guidance for high-pressure synthesis. Also the problem of retention of phases, formed in high-pressure synthesis, upon the release of pressure will be discussed.

1. ENHANCEMENT OF PHASE-TRANSFORMATION RATES BY APPLICATION OF PRESSURE

The frequency of a kinetic process can be considered to consist of the product of a thermodynamic and a kinetic factor. The thermodynamic factor is some function, $f[\Delta G(P,T)]$ of the Gibbs free energy change $\Delta G(P,T)$ accompanying the process and it is expected to vary rather slowly with pressure. Considered here are kinetic effects so large that they imply marked increases in the kinetic factor $k_i^\bullet(P,T)$ with pressure. Examples are the large pressure enhancements of crystal growth rates in amorphous B_2O_3[2,3] and SiO_2[4] at quite low temperatures and in transformations generated by shock waves. The pressure effects on the crystallization of amorphous B_2O_3 are especially striking. At low pressure even seed

crystals which have been melted back fail to grow at measurable rates in the undercooled region. However, substantial growth occurs even at quite low temperatures upon application of 10 to 30 kbars of pressure.

It has been found that the kinetic time constants for crystal growth usually scale roughly as the shear viscosity of the melts into which the crystal is growing. Since the activation volumes for viscous flow are generally observed to be positive, the marked pressure enhancements of crystal growth were quite unexpected. Three sorts of explanations have been offered for these effects. The first explanation is that the structure of the melt changes with increasing pressure to configurations more conducive to crystal growth. The second explanation is that the increase in driving free energy due to pressure application markedly increases the fraction, f, of growth sites in the crystal surface.[5] The effect of pressure on f could be marked if there were large potential barriers to monolayer nucleation on the surfaces of the crystal normal to the growth direction. In the simple theory for two-dimensional nucleation, the parameter which largely determines this barrier is σ_e, the edge tension of the monolayer in contact with the melt. Increasing pressure could change the melt structure in a way such that σ_e would be reduced or it might increase $|\Delta G|$ with the result that the barrier to two-dimensional nucleation would decrease--in particular, the radius, r^*, of the critical monoloyer is $r^* = -\frac{\sigma_e \bar{V}}{\Delta G}$ and the thermodynamic barrier to monolayer nucleation is $\pi \lambda r^* \sigma_e$ where $\bar{V}$ is the molar volume of the crystal and λ is the monolayer height. Finally the third explanation main-

tains that impurities catalyzing crystal growth might be re-
tained in larger concentrations at the higher pressures.

a. Effect of Pressure on Melt Structure: As pressure
is increased, systems tend to evolve toward structures
in which the binding is less directional and the number of
nearest neighbors is increased. In this evolution the
nearest neighbor separation might also increase but the
effect of this on specific volume would be more than offset
by the increased coordination number. Thus, covalently bound
systems tend to be transformed by increasing pressure
into structures with binding that is more ionic or
metallic in nature. The atomic mobility in the liquid
states of these systems, owing to the greater interatomic
separations and non-directional binding, is likely to
be much greater than in covalently bound liquids at
equivalent specific volume and composition. Crystal-
growth kinetic constants are expected to be similarly
scaled.

By this mechanism the resistance to crystal growth
in a molten state, in which the binding was mostly covalent
initially, might be decreased markedly by application of
high pressure. As has been recognized, this effect may
account for some of the anomalously high rates of trans-
formation produced by shock waves. It may also be an
important factor in the lowered resistance of fused
silica to crystallization at high pressure. However,
the similar effect in B_2O_3 may be more complicated in
view of the large apparent disparity between resistances
to melting and crystal growth in B_2O_3 at ambient pressures.

b. Effect of Pressure on Fraction of Surface Growth Sites:

Some possible phenomenological causes for the effect of pressure on the growth-site fraction, f, have been indicated already. If screw dislocations emerge in the surface of the growing crystal the growth-site density/area will scale approximately at $\frac{1}{r^*}$, meaning that a relatively large value of σ_e can lead to a slow growth rate even if the crystal is imperfect. On the other hand, the melting-site fraction, and hence the melting rate, can be much greater than the corresponding quantities for growth, owing to the finiteness of the crystal surface area. Thus, the growth and melting behavior of B_2O_3 at the ambient pressure might be explicable in terms of a relatively large σ_e for this system. Application of pressure might reduce σ_e by effecting some change in structure of the melt (e.g., the "boroxyl" type of short-range order suggested for B_2O_3 glass by Mozzi and Warren[6] might transform to a type of short-range order more similar to that in B_2O_3 crystals; also r* might fall with increasing pressure due to the concurrent increase in $|\Delta G|$).

c. Retention of Catalyst Impurities at High Pressure:

High pressures may be applied to extend greatly the range of compositions at high densities in monophase systems. Such systems often are especially well adapted to rapid growing of crystals with satisfactory perfection. One of the best known of crystal-growing techniques of this type is hydrothermal crystallization.[7] In this method a high temperature solubilizes the crystal nutrient in a fluid medium while the application of pressure maintains the medium at a high density.

It is possible that similar growth processes may
occur at high pressure when the amount of solvent is
small relative to that of the crystallizable material,
CM. For example, suppose that at high temperature and
pressure the binary system H_2O-CM can phase separate into
nearly pure CM and a concentrated fluid solution of CM
in water. Then a concentrated H_2O-CM solution could form
from a very small amount of water and serve as a medium
for rapid transport of CM from some metastable to a more
stable crystalline state. Similar processes can occur
at the ambient pressure (e.g., in the devitrification of
GeO_2 glass, when the solubility of CM in H_2O is high
enough).

Impurities either localized or adsorbed at inter-
face also may catalyze crystal growth, especially in
covalently bound systems, without the separation of an
impurity-rich fluid phase. Application of high pressure
can lead to the retention of high concentrations of these
impurities to much higher temperatures than would be per-
mitted at low pressure. This provides an additional
mechanism for the pressure enhancement of crystal growth
rate.

2. RETENTION OF PHASES SYNTHESIZED AT HIGH PRESSURE

Phases, β, formed by application of high pressure
may revert to the initial low-pressure, α, phase by nucleation
and growth or by a spinodal mechanism.[8] Spinodal reversion
might occur if the new structure developed a compositional or
a shear instability upon removal of the pressure.

It would be extremely difficult to eliminate the
heterogeneities, impurity particles, and imperfections, that

might serve as centers for a nucleation and growth reversion
of β to α. Consequently, the most practical approach to the
problem of retaining phases synthesized at high pressure is
to find conditions in which the rate of growth from the α
nucleation centers, or, in spinodal decomposition, the ampli-
fication rate of fluctuations, is negligible. If the kinetic
factor in the growth or amplification process is thermally
activated, it should be possible, in principle, to select
for the pressure release a temperature that is low enough so
that the β will be retained. However, there are a number of
"shear-type" transformations, especially in metal systems,
in which the propagation or amplification process apparently
requires no thermal activation. In the event that such a
shear mode is possible for the reversion of β to α, it would
seem difficult, if not impossible, to retain β, at least in
substantial quantities, after the pressure release.

It is interesting to consider the problem of the retention
of a metallic phase of hydrogen if it were synthesized. It
appears that one of the main mechanisms of decomposition of
this phase would be the association of hydrogen atoms at the
surface. This process would ultimately be limited by the
frequency of dissociation of atoms from surface kink sites.
The number of atomic layers/time, $\dot{n}$, evaporated by this
mechanism might be specified approximately by

$$\dot{n} \sim f\nu e^{-\epsilon/kT}$$

where f is the fraction of kink sites in the surface, ν is a
vibration frequency, and ϵ is the energy required to dissociate
an atom from a kink site. Setting $\nu f \sim 10^{12}$ sec^{-1} the con-
dition that $\dot{n}$ not exceed 1/sec is that $T \overset{\sim}{<} \frac{\epsilon}{28k}$. The magnitude

of ϵ is difficult to estimate, but it seems unlikely that it
would exceed $\frac{1}{2}$ of the cohesive energy/atom of metallic hydrogen.

REFERENCES

1. See, for example: J. E. Hilliard and J. W. Cahn, "Progress
   in Very High-Pressure Research," p. 109 (edited by F. P.
   Bundy, W. R. Hibbard, Jr., and H. M. Strong), Wiley &
   Sons, New York (1961); R. E. Hanneman, "Reactivity of
   Solids," p. 789 (edited by T. W. Mitchell, R. DeVries,
   R. W. Roberts, and P. Cannon), Wiley & Sons, New York (1969);
   R. S. Bradley, J. Inorg. Nucl. Chem., 33, 1969 (1971).

2. F. Dachille and R. Roy, J. Am. Ceram. Soc., 41, 78 (1959).

3. J. D. MacKenzie and W. F. Claussen, J. Am. Ceram. Soc.,
   44, 79 (1961).

4. D. R. Uhlmann, J. F. Hays, and D. Turnbull, Phys. and Chem.
   Glasses, 7, 159 (1966).

5. D. R. Uhlmann, J. F. Hays and D. Turnbull, Phys. and Chem.
   Glasses, 8, 1 (1967) [this paper also reviews earlier
   literature on the problem].

6. R. F. Mozzi and B. E. Warren, J. of Appl. Cryst., 3,
   251 (1970).

7. R. A. Laudise and J. W. Nielsen, Solid State Physics, 12,
   pp. 149-220, Academic Press, N. Y. (1961).

8. For review of spinodal mechanisms see: J. E. Hilliard,
   "Phase Transformations," pp. 497-560, Am. Soc. Metals,
   Metals Park, Ohio (1968).

APPENDIX G

SUPERCONDUCTIVITY*

by C. W. Swenson**

Iowa State University, Ames, Iowa

Superconductivity is of technological interest because of the possible use of superconducting components in such diverse areas as power transmission lines, electric motors and generators, magnetic bottles for power generation by fusion, and high-speed ground transportation.[1] Existing superconductors must be kept at temperatures near the boiling point of liquid helium ($4°$ K, $-269°$ C, $-452°$ F) if they are to be used in these applications, and refrigeration problems become important.

Hence, one concern of modern superconductivity research is the discovery of superconductors with ever high-transition temperatures and two approaches may be defined. The first uses qualitative theoretical guidelines and empirical rules in survey-type investigations of metallurgical systems.[1,2,4] The highest known superconducting transition temperature of $21°$ K (for $Nb_3(Al_{0.75}Ge_{0.25})$) was discovered, or more correctly, was produced in an investigation of this type.[1] A second approach attempts to understand the basic

---

* This general discussion of superconductivity and the role high pressures have played in superconductivity research is based in part on a number of recently published general articles.[1-4] These articles should be consulted for details and additional references.

** In consultation with T. H. Geballe of Stanford University.

mechanisms that bring about superconducting behavior with the
hope that these can be used to predict either favorable con-
ditions for high transition temperatures or to set fundamental
limits for the occurrence of superconductivity. To some extent
the two approaches are concerned with quite different types of
systems, since the empirical approach tends to concentrate on
relatively complex systems similar to those for which high
transition temperatures have been observed, while the more
theoretical approach must make its beginnings in the under-
standing of relatively simple, often purely elemental, systems.

High-pressure methods have played an important role
in both of these types of investigations. The experimental
methods used have been surveyed by Brandt and Ginsburg[3] who
reference both their own and other Russian work as well as
work done in the United States and other countries. Matthias'
survey article,[2] which appears in a special low temperature
issue of Physics Today (August, 1971), outlines the current
status of superconductivity research and the semi-empirical
search for ever higher transition temperatures. His survey
shows that the superconductivity of a number of the elements has
been discovered only through the use of high-pressure techniques
and that phase transitions can produce a material which is a
superconductor only at high pressure. This is the case for
the semiconductor-metal transitions of germanium and silicon,
for instance, and for transitions in which magnetically
ordered phases are destroyed (such as for cerium), while
cesium is the first normally monovalent metal which has been
shown to be a superconductor. Matthias[2] makes the interesting,
challenging, and broad comment that "Many elements have become
superconducting under pressure but none has ever lost this
property yet!"

However, not all high-pressure modifications of the
elements have been investigated for superconductivity. Typical
examples are iodine (which has a semiconductor-metal transition),
rubidium, and potassium (which have unusual high-pressure
modifications), chromium (for which a special type of magnetic
ordering disappears under pressure), and the rare earth metals
(which have electronic transitions at high pressure to what
could be non-magnetic phases). One of the challenges is that
no definite predictions can be made as to whether or not a new
phase will be superconducting. The experiments are difficult
and require pressures of up to several hundred kilobars at
temperatures of less than 1° K. Apparatus of this type has
been designed and used for some applications.[3]

High-pressure methods can be used to generate
superconducting modifications of solids which remain stable
when the pressure is released, although often only at low
temperature. Brandt and Ginsburg[3] give several examples,
including metallic indium antimonide, antimony, and bismuth.
The alloys of the yttrium-thorium sesquicarbide system,[5]
which can be produced only at high pressure and high tempera-
ture, are stable at low pressure and are particularly interest-
ing since they show a systematic variation of the superconduct-
ing transition temperature with lattice parameter with a
maximum at 17.6° K. The low-pressure stability of a given
compound that can be produced only under pressure cannot be
predicted beforehand, and indeed this is a major unanswered
question common to all high-pressure syntheses.

One of the most important objectives of work in
this area is the understanding of the basic mechanisms

leading to superconductivity. Many phenomena are explainable
in terms of the electron-phonon interaction and the BCS theory,
but feelings often are expressed[2] that different mechanisms
must exist to explain the occurrence of superconductivity in
various cl sses of metals. Non-transition metals (such as
tin, lead, and indium) appear to be BCS-like and are said to
be "understood." The transition elements (niobium, tantalum,
and vanadium, for instance) may belong to another distinct
category, while the rare earth-type metals (lanthanum, cerium,
yttrium, and possibly uranium) show somewhat different behavior.
Why is lanthanum a superconductor with a relatively high tran-
sition temperature (5° K), yttrium a superconductor only under
pressure, and scandium never a superconductor? The high-pressure
measurements of the superconducting transition temperature for
lanthanum[6] must be considered in answering this question since
they show a variation which is anomalous both in sign (the
transition temperature rises with increasing pressure) and in
magnitude (an increase from 5° K to 12° K in 140 kbar). The
increase appears to be linear in volume to a first approxima-
tion for the 25% volume change of these experiments. Lanthanum
represents an extreme case; yet transition metals in general
show quite different pressure effects from non-transition
metals. There are no ground rules to use in determining the
region of stability of the superconducting state, although
Brandt and Ginsburg[3] suggest that both zinc and cadmium should
become normal metals at very high pressures at absolute zero.
What is a valid extrapolation procedure? Any phase transitions
that occur can be expected to affect the transition temperature,
and Matthias[2] suggests a general tendency towards increase.
Experiments designed to establish or differentiate between

various mechanisms for superconductivity are badly needed,
as are theories that can suggest such critical experiments.

The major concern in the above paragraph would
appear to be in the relatively simple elemental superconductors
for which theories can be proposed. Most of the high-temperature
superconductors that have technological applications are more
complex, and it is not clear that the same considerations will
apply. For instance, Geballe[1] has suggested that transition
temperatures greater than 12° K occur mostly in materials that
have lattice instabilities. Many of these (such as Nb_3Sn)
have the cubic beta-tungsten structure in which there are un-
broken linear chains of the transition metal ions. This one-
dimensional structure appears to be very important for super-
conductivity, and Smith[7] recently has reported on a systematic
investigation of pressure effects on the superconductivity of
many of these compounds in an attempt to test various theories,
with inconclusive results. Various layer-structure chalcogenide
compounds have been discovered recently to be superconducting[1]
in a manner which appears to be two-dimensional. The complexity
of these effects is evident not only in the rapid rise of T_c
with pressure as has been observed for $NbSe_2$,[8] but also by
the discovery of high superconducting transition temperatures
(10 to 13° K) for ternary alloys of similar compounds[9] which
are of the form $Li_xTi_{1.1}S_2$. Any mechanisms proposed for super-
conductivity in these materials certainly must predict the
results of high-pressure measurements.

The above survey then suggests several potentially
profitable applications of high-pressure techniques to research
on superconductors including:

(1). Routine testing of new high-pressure metallic
modifications of all solids for superconducting behavior,
and the systematic study of promising ternary systems.
Particular emphasis should be given to systems which are
metastable at low pressure since apparently metastability
is important for high transition temperatures. While the
mass production high-pressure synthesis of superconducting
materials may never be feasible economically, these studies
should be encouraged since they can give guidelines as to
the existence of other, more easily produced materials.
A portion of the above program should be devoted to studies
of the high-pressure modifications of the elements that
have not been tested for superconductivity, since in this
case the role of crystal structure is most clearly evident,
and theoretical calculations could be possible.

(2). Systematic studies of the effects of high pressure
on the superconductivity of existing systems (such as the
study carried out by Smith[7]). Such studies could make
particularly valuable contributions to our understanding
of superconductivity, initially through correlations and
ultimately through direct tests of theories. Theoretical
work is needed that can suggest critical experiments which
can be used to differentiate between various mechanisms.

(3). An investigation of the effects of defect structures
on superconducting behavior. Very little is known about
these effects. The superconducting transition temperature
of TiO[10] for instance has been increased from 1° K to over
2° K by a high-pressure anneal in which the vacancies in
the as-grown normal crystal are squeezed out. Similar
effects should be observed for other compounds such as NbN.

REFERENCES

1. T. H. Geballe, Sci. American, 225, No. 5 (Nov.), 22 (1971).

2. B. T. Matthias, Physics Today, 24, No. 8 (August), 21 (1971). (This issue of Physics Today contains two other articles -- on Josephson junctions and on superconducting magnets -- which also are of interest.)

3. N. B. Brandt and N. I. Ginsburg, Sci. American, 224, No. 4 (April), 83 (1971); Contemp. Phys.,10, 355 (1969).

4. B. T. Matthias, Amer. Scientist, 58, 80 (1970).

5. M. C. Krupka, A. L. Giorgi, N. H. Krikorian, and E. G. Szklarz, J. Less Common Metals, 19, 113 (1969).

6. M. B. Maple, J. Wittig, and K. S. Kim, Phys. Rev. Letters, 23, 1375 (1969).

7. T. F. Smith, J. Low Temp. Phys., 6, 171-95 (1972).

8. D. Jerome, A. J. Grant, and A. D. Yoffe, Solid State Comm., 9, 2183 (1971).

9. H. E. Barz, A. S. Cooper, E. Corenzwit, M. Marezio, B. T. Matthias, and P. H. Schmidt, Science, 175, 884 (1972).

10. N. S. Doyle, J. K. Hulm, C. K. Jones, R. C. Miller, and A. Taylor, Phys. Letters, 26A, 604 (1968).

APPENDIX H

FERROMAGNETIC MATERIALS

by George A. Samara

Sandia Laboratories, Albuquerque, New Mexico

Much of the high-pressure work on ferromagnetic
(FM) materials has been aimed at a better understanding of the
physical phenomena involved and was motivated by the early
recognition that the exchange forces which govern ferromagnetism
are strong functions of interionic distances. In principle,
the variations of the magnetization (or magnetic moment) and
the Curie temperature T_c with pressure reflect important
changes in the inter- and intra-atomic interactions. In
practice, however, these exchange interactions are fairly
complicated and generally not understood, especially in the
case of metals, and progress towards the better fundamental
understanding has been somewhat limited. Nevertheless, the
use of high pressure in FM materials science and technology
has been and will continue to be an important and fruitful
endeavor.

A few pertinent points covering both science and
applications are commented on here. These comments are in-
tended to complement Goodenough's contribution, Appendix J,
and are restricted to ferro- and ferrimagnetic substances.
Pressure studies on antiferromagnetic and paramagnetic
materials are of much scientific interest but will not be
considered here.

1. <u>FM MATERIALS RESEARCH</u>

<u>a</u>. <u>Insulators</u>: Insulators are the simplest FM materials.
Here the inter-atomic exchange forces are of the direct,
indirect, or superexchange type, and the effects of
pressure on the magnetic properties are qualitatively
and, in some cases, semiquantitatively understood. Good
examples are ferrites ($MeO \cdot Fe_2O_3$) and garnets ($3Me_2O_3 \cdot 5Fe_2O_3$), where Me is a transition metal ion. Though
complicated both chemically and structurally, these
materials are rather simple magnetically. The dominant
interactions are of the superexchange type operating
between neighboring magnetic ions via the intermediate
oxygen ions. The strength of the interactions is pro-
portional to the amount of overlap between the $3\underline{d}$ wave
functions of the metal and the $2\underline{p}$ wave functions on the
adjacent oxygen. This overlap should increase with
pressure and the Curie (or Néel) temperature can be ex-
pected to increase. Indeed that is what is observed
experimentally with dT_c/dP typically in the range 1-2° K/
kbar. In many of these substances the magnetic moment
per unit mass has its spin-only value and should not be
affected by pressure. This has been confirmed by experi-
ment (e.g., yttrium iron garnet and magnetite).

In the presence of anisotropic (nonhydrostatic)
stress, strain-induced magnetic anistropy effects can
become important especially for materials with large
magnetostriction. This anistropy induces an easy direc-
tion of magnetization which can be different from the
applied magnetic field direction and thus competes with

the field. For low values of the applied field the mag-
netization can rotate away from the field direction towards
the easy direction. Materials such as nickel ferrite
exhibit strong strain-induced anisotropy effects, and
these are reflected in the large rotations in magnetiza-
tion at low fields observed in shock-wave compression
experiments in the elastic range. In this range the stress
is anisotropic.

b. Metals: In the case of FM metals interactions between
conduction electrons and magnetic spins are complicating
factors, and the question of the localized versus the
itinerant nature of the magnetic moment remains generally
unresolved. Although the pressure results on the magnetic
properties of these metals are usually difficult to in-
terpret, they remain important. This is especially so in
cases where the results might be used to assess the validity
of an existing model or perhaps to choose between competing
models. Two examples of recent work, which may come close
to achieving this goal, serve to illustrate the point.

(1) $ZrZn_2$

This is thought to be perhaps the best example
of a weak itinerant ferromagnet. It has a small
magnetization and a low Curie temperature ($\sim 20°$ K)
which decreases with pressure. The initial decrease
is linear with a slope $dT_c/dP = - 1.9°$ K/kbar.
Recent results[1] have shown that the decrease con-
tinues to be linear up to $\sim$ 7.5 kbar and then T_c
decreases rapidly to zero, the FM state vanishing
for pressures $> \sim$ 8.5 kbar. At present this is

the only known example of the vanishing of ferromagnetism at high pressure and $0°$ K. The observed pressure dependence of T_c has been discussed[1] in terms of a model for weak itinerant ferromagnets,[2] and, in fact, such a model is capable of qualitatively reproducing certain aspects of the experimental results. In particular the model predicts a decrease of T_c with pressure and that $(dT_c/dP) \rightarrow -\infty$ as $T_c \rightarrow 0°$ K, as observed. Careful examination of the results, however, shows that the initial linear decrease of T_c extends to a much higher pressure than is predicted by the simple model.[1,3] It may be possible to give a better account of the results by a model that combines an itinerant and a localized description--a so-called modified Zener model.[3] This model is essentially an itinerant one but with some localized character. It does away with the neglect of Hund's rule effects and degeneracy of the $\underline{d}$ bands effects which are assumed in the simple itinerant model and deemed objectionable.

(2) Invar Alloys

Face-centered cubic iron-nickel alloys in the Invar region ($\sim$ 25-45% Ni) exhibit many anomalous properties including large decreases in magnetization and Curie temperature with decreasing Ni content, large volume magnetostriction, negative thermal expansion at low temperature, and large compressibilities. In agreement with the predictions of the weak itinerant model, their magnetizations and Curie temperatures exhibit large

decreases with increasing pressure. This behavior combined with observations that many of their atmospheric pressure properties are consistent with this model have led to the belief that these materials are weak itinerant ferromagnets. Recent extensions of the pressure measurements to much higher pressures for some of these alloys have, however, yielded results not consistent with the simple itinerant model.[4] In particular T_c decreases linearly over a large pressure range with indications that vestiges of the FM state will persist to very high pressures (i.e., the FM state may never vanish). It appears that the results can be described by the modified Zener model mentioned above.[3] It must be emphasized, however, that this description as well as that for $ZrZn_2$ is rather phenomenological in that it does not incorporate any details of the electronic structure of these materials--details that must certainly be important. Unfortunately our present knowledge of these details is either primitive or nonexistent, and phenomenological treatments can be quite useful in correlating and examining trends in experimental data.

High-pressure results of the type described above for the Invar alloys and $ZrZn_2$ constitute significant knowledge which should ultimately enhance our understanding of ferromagnetism in metals. It is in studies of this kind, and on select materials, that high pressure can be expected to have an impact on this field.

2. APPLICATIONS

Some of the possible direct applications of high pressure in magnetic materials science and technology are discussed by Goodenough. In addition to these, there are some unique applications that deserve brief mention. These are based on pressure-induced changes in magnetization and can be utilized specifically under shock-wave conditions. Examples are FM shock-wave stress gages and electrical power sources. The power sources are capable of producing relatively large current or voltage pulses in a manner similar to the ferroelectric power sources described elsewhere in this report. The electrical pulse results from the pressure-induced change in magnetic flux detected by a pick-up coil wound on the FM material.

The change in magnetization with compression results from any of the following causes: (a) an intrinsic change in magnetic moment or a shift of the Curie temperature with pressure, or both; (b) a pressure-induced phase transition to a nonferromagnetic phase or to an FM phase of different magnetization; or (c) a strain-induced magnetic anistropy.

ACKNOWLEDGEMENT

REFERENCES

1. T. F. Smith, J. A. Moydosh, and E. P. Wohlfarth,
   Phys. Rev. Letters, 27, 1732 (1971).

2. E. P. Wohlfarth, J. Appl. Phys., 39, 1061 (1968);
   J. Phys.,C 2, 68 (1969).

3. L. C. Bartel, Phys. Rev., B, (accepted for publication)
   and private communication.

4. L. C. Bartel, L. R. Edwards, and G. A. Samara, Proc.
   Magnetism and Magnetic Materials Conference (1971),
   American Institute of Physics, p. 482.

APPENDIX I

DIELECTRIC AND FERROELECTRIC MATERIALS
AND APPLICATIONS

by George A. Samara

Sandia Laboratories, Albuquerque, New Mexico

The use of pressure in the study of dielectric and
ferroelectric materials has made contributions in three general
areas: (1) basic understanding, (2) materials synthesis and
fabrication, and (3) device applications. Much of the work
has been devoted to the first and second areas and significant
contributions have been achieved. Device applications, on
the other hand, have been rather limited since they are
generally restricted to very low pressures or unique environ-
ments. In this appendix the present status of the field will
be assessed and certain aspects of the above areas and con-
tributions will be discussed.

1. EFFECTS OF PRESSURE ON DIELECTRIC AND FERROELECTRIC
   PROPERTIES

a. Introduction

The interatomic forces and interactions which deter-
mine the structure and properties of matter are strong functions
of interatomic separation (and volume), and, therefore, pressure
is a fundamental variable in the study of physical properties.
Results of pressure experiments lead to a better understanding
of these properties and often make it possible to test the
validity of theoretical models. It is in this general context
of understanding physical properties that high-pressure work
has its greatest impact (though perhaps indirect) on dielectric
materials science and technology. The direct use of pressure in

material synthesis and in device applications, though some-
times unique and important, will always be more limited.

Pressure studies are necessary and sometimes essen-
tial for understanding physical properties and, in particular,
the temperature dependence of a given material property. The
measured change in property with temperature at constant
pressure arises from two contributions: (1) the change that
arises solely from the change in lattice spacing or density
(i.e., the explicit or pure volume effect), and (2), the
explicit or pure temperature effect that would be present
even if the volume of the sample were to remain fixed. Iso-
thermal pressure measurements give the pure volume effect
directly and thus make it possible to evaluate the two con-
tributions to the isobaric temperature measurements. The
pure temperature contributions arise from anharmonic lattice
effects, and as shall be pointed out later, play predominant
roles in ferroelectrics and certain dielectrics.

In addition to the above-mentioned volume effects there
are some property changes unique to the high-pressure environ-
ment. Most important among these are a wide range of pressure-
induced phase transitions which are accompanied by large, often
drastic, changes in physical properties. For example, dielectrics
(=insulators) may become good semiconductors or metals, normal
dielectrics may become ferroelectrics, and ferroelectrics may
lose their spontaneous polarization and become normal dielectrics.
In addition to their scientific interest such changes have
applied implications.

b. Dielectrics

Comments here shall be restricted largely to the
effects of pressure on the dielectric constants. Other impor-
tant aspects such as optical properties and electrical con-

ductivity are treated in another section of this report. A knowledge of the static (ϵ_s) and high-frequency (ϵ_∞) dielectric constants of a substance and their temperature and pressure dependences is of great interest because these properties enter into the treatment of and/or determine various physical properties (e.g., problems of electron-electron and electron-phonon interactions and dispersion, optical properties, and effective field considerations). Such important properties of dielectrics as the capacitance, dielectric loss or Q factor, dielectric strength, electrical transport, optical refraction, electro-optical effects, and laser beam-medium interactions are determined, or strongly influenced, by these dielectric constants. Future progress in the development of high energy storage capacitors, nonlinear dielectrics, and improved piezo-electrics can be strongly influenced by a better knowledge of electric polarization phenomena. Three sources of polarization are induced by the application of an electric field to a dielectric. These are (1) electronic, (2) ionic, and (3) dipolar. Electronic polarization results from the displacement of the electron distribution relative to the nucleus for each atom or ion and thus produces an electric dipole moment. Ionic polarization, on the other hand, is caused by the opposite displacements of positive and negative ions from their equilibrium positions. This mechanism of polarization is operable in the infrared and lower frequency regions. At higher frequencies the ions cannot follow the variation in electric field, and the ionic polarization vanishes. Dipolar polarization comes into play at sufficiently low frequencies and is associated with substances made up of molecules that possess a permanent electric dipole moment or with substances containing dipolar impurities.

(1). <u>High Frequency Dielectric Constant</u>: The high-frequency dielectric constant is determined by electronic polarization and is given by $\epsilon_\infty = n^2$, where n is the index of refraction. The electronic polarizability α_{elec} is determined by the electronic structure of the ion or atom, and its value can be calculated, in principle, from a solution of the differential equations of motion for the perturbation by an external field of the electronic wave functions for the various electronic shells. This is a complex theoretical problem even in the free ion or atom because of the quantum and many-body nature of the interactions; it is further complicated in the case of ions and atoms in condensed media where added inter-actions and distortions of the electronic distributions occur. Theoretical calculations are most successful for the smallest (containing fewest number of electrons) atoms and ions and become less satisfactory for the larger ones. Because of the complexity of first prin-ciples calculations, however, it has proved very useful, at least in the case of ionic crystals, to determine empirical values of the electronic polarizabilities of ions from measured values of the index of refraction. This is generally done on the basis of the additivity rule (i.e., the total α_{elec} is taken as the sum of the individual polarizabilities of the constituent ions). Refinements which introduce the effect of the lattice environment on the individual α's have also been made, and tabulated values of electronic polarizabilities are available and widely used.[1,2]

Changes in the refractive index of a substance with temperature and pressure (or stress) can result

from changes in (a) the Coulomb and local fields in the medium, (b) the density of the medium, and (c) the intrinsic α_{elec}'s of the constituent ions or atoms. For isotropic dielectrics and uniform stress (a) is negligible; however, for anisotropic substances and/or nonuniform stress, changes due to (a) have to be taken into account.

An examination of data on a wide variety of isotropic dielectrics shows that the pressure (P) and temperature (T) derivatives of n (or ϵ_∞) can be either positive or negative.[3,4] For example, (dn/dT) is negative for the alkali halides and positive for diamond and MgO, whereas (dn/dP) is positive for the alkali halides and negative for diamond and MgO. The effects due to the change in density can be readily understood: n increases with increasing density of polarizable entities. Analysis of the pressure results shows that in all cases the electronic polarizability increases with increasing volume, i.e., $(\partial\ln\alpha_{elec}/\partial\ln V)_T$ is positive. This means that α_{elec} decreases with increasing pressure leading to a negative contribution to the pressure dependence of n and ϵ_∞. This is what one might intuitively expect. The distortion of an ion (and thus its polarizability) in an electric field becomes smaller when the space available for distortion (i.e., the volume) becomes smaller. In the case of the alkali halides the increase in density dominates and n increases with pressure and decreases with temperature. For diamond and MgO the opposite is true with $(\partial\ln\alpha_{elec}/\partial\ln V)_T$ dominating. In all cases, except diamond, the volume-independent, or pure temperature contribution, $(\partial\ln\partial_{elec}/\partial T)_V$, to dn/dT

is very small and negligible. This is an important
conclusion with practical as well as scientific implica-
tions -- it means that to a good approximation, α_{elec} is
a function of volume only. Thus, knowing either the
temperature or pressure dependence of n we can estimate
the other provided, of course, that the compressibility
and thermal expansion are known. For diamond the pure
temperature contribution, though small, is comparable
in magnitude to the pure volume effect and cannot be
neglected.

(2). The Static Dielectric Constant: The values of the
static dielectric constant ϵ_S of normal ionic crystale (i.e.,
nonferroelectrics) varies from ~(4 to 5) up to several
hundred. A comparison between values of ϵ_S and the high-
frequency constant ϵ_∞ shows that ϵ_S is much larger. Thus,
for example, for NaCl ϵ_S = 5.90 and ϵ_∞ = 2.33 and for
rutile (TiO$_2$, c-axis) ϵ_S = 166 and ϵ_∞ = 7.2. The differ-
ence $\epsilon_S - \epsilon_\infty$ is a measure of the lattice (ionic) con-
tribution to the dielectric constant (i.e., a measure
of the lattice or infrared polarizability). This impor-
tant mechanism of lattice polarization arises from
opposite displacements of positive and negative ions in
the presence of an electric field, and thus has its
origin in the lattice vibrations of the crystal. Its
treatment is a problem in lattice dynamics. The general
theoretical treatment is complicated by the fact that
lattice vibrations are not completely harmonic, and the
introduction of high-order anharmonic potential and
dipole moment terms makes an exact solution of the
problem impossible. One of the benefits of pressure

studies is that they make it possible to estimate the anharmonic contribution to the isobaric temperature variation of ϵ_S. In some crystals such as rutile, these contributions dominate and, as shall be seen later, play an all important role in ferroelectrics.

Theoretical models show that for ionic crystals ϵ_S is determined by the infrared resonance frequency of the crystal and the ionic charge as well as ϵ_∞. Comparisons between calculated and experimental values of ϵ_S for many crystals show that the ionic charge does not have its formal value of Ze, where Z is the valence. For this purpose the concept of an effective ionic charge Ze* has been introduced.[5] In the ideal case of deformable ions that do not overlap, the ratio e*/e is unity. In real solids, however, the ions overlap, and the concept of an effective ionic charge serves to account for the polarization effects associated with the overlap. Deviations of e*/e from unity arise from three effects: (a) short-range repulsive interactions between the electron clouds on adjacent ions which modify the electronic dipole moments, (b) redistribution of charge and overlap when the ions move in the course of lattice vibrations, and (c) modification of the local electric field at a given lattice site by the distortion of neighboring ions. Using the earlier examples, analysis of experimental data including pressure measurements shows that e*/e $\approx$ 0.77 for NaCl and 0.64 for rutile.

High pressure measurements of ϵ_S for ionic crystals can be used to determine the magnitude of the anharmonic contribution to ϵ_S and to obtain better values of e*/e

than those which were based on a completely harmonic model, reported in the earlier literature. This can be seen simply in the following way: ϵ_S is given by[5]

$$\epsilon_S - \epsilon_\infty = \frac{4\pi (Ze^*)^2}{\mu V \omega_{TO}^2} \left(\frac{\epsilon_\infty + 2}{3}\right)^2 + G$$

$$= \eta + G \quad , \quad\quad\quad (1)$$

where μ is the reduced mass, V is the volume per molecule, and ω_{TO} is the IR resonance frequency. The term denoted by η is the lattice contribution to ϵ_S in the harmonic approximation and G represents the anharmonic contributions. G is a complicated function, but in the high temperature limit (i.e., for $T > \theta_D$), it reduces to

$$G = T[\partial(\epsilon_S - \epsilon_\infty)/\partial T]_V \approx T(\partial\epsilon_S/\partial T)_V . \quad (2)$$

The right-hand side, and therefore G, can be readily evaluated from the measured pressure and temperature dependences of the dielectric constants, and then e* is calculated from Eq. 1 using appropriate values for the other variables. G can be quite large, for example, at 300° K G amounts to 3-10% of the lattice dielectric constant, $(\epsilon_S - \epsilon_\infty)$, in the case of the alkali halides, over 30% in the thallous halides, and over 40% in rutile.

A very useful relationship in the study of the dielectric properties of ionic crystals in the Lyddane-Sachs-Teller (LST) relationship. It is based on the harmomic approximation, and for diatomic crystal, takes the simple form

$$\frac{\epsilon_s}{\epsilon_\infty} = \left(\frac{\omega_{LO}}{\omega_{TO}}\right)^2 , \tag{3}$$

where ω_{LO} is the long wavelength longitudinal optic
phonon frequency. From Eq. 3 it is seen that large
values of ϵ_s can be associated with small values of
ω_{TO}. This has an important implication in the case
of some ferroelectrics for which it is now established
that $\epsilon_s \to \infty$ and $\omega_{TO} \to 0$ as the temperature approaches
the transition or Curie temperature.

The effects of pressure and temperature on ϵ_s
have been determined for a large number of dielectrics.[6-8]
As was the case for ϵ_∞, both positive and negative
values of $d\epsilon_s/dP$ and $d\epsilon_s/dT$ are observed. Analysis of
the data in terms of the pure volume and pure temperature
contributions to $\epsilon_s(T)$ is quite revealing and has led
to some deeper insight and generalizations concerning
the dielectric properties of solids. Particularly
interesting are the changes in behavior as ϵ_s increases
in value for different solids. In general, $d\epsilon_s/dT$
starts out positive for small ϵ_s (e.g., NaCl, $\epsilon_s = 5.9$)
and becomes increasingly more negative as ϵ_s increases
(e. g., TlBr, $\epsilon_s = 30.4$ and c-axis rutile $\epsilon_s = 166$).
Since, in general, ϵ_s decreases with increasing pressure
reflecting the fact that the ionic polarizability
decreases with decreasing volume (i.e., the solid
becomes stiffer) despite the increase in density, the
above trend in $d\epsilon_s/dT$ reflects an increase in the in-
fluence of the pure temperature effect $(\partial\ln\epsilon_s/\partial T)_V$ as

ε_s increases. As mentioned earlier, this pure temperature contribution arises from anharmonicities in the crystal potential and dipole moment. It is also found that the sign of $(\partial \ln \varepsilon_s / \partial T)_V$ depends on crystal structure (e.g., it is positive for crystals having the NaCl structure and negative for crystals having the CsCl structure). This reflects important differences in the nature and origin of the anharmonicities in different crystal structures. These differences, however, are not well understood.

Much information about anharmonic interactions in dielectrics can be gained from detailed studies of the pressure and temperature dependences of vibrational spectra. Particularly important from the standpoint of the dielectric response is the behavior of the IR resonance frequency ω_{TO} in Eq. 1. Pressure measurements on ω_{TO} have been performed on a number of ionic crystals using far IR techniques.[9] Unfortunately, the accuracy of the data thus far has been limited. Accurate measurements are important, since a knowledge of the pressure dependence of ω_{TO} combined with the pressure dependences of ε_s and ε_∞ allows one to determine the pressure or volume dependence of the effective charge. At present, values of $(\partial \omega_{TO} / \partial P)_T$ are generally not known accurately enough to allow this, since $(\partial \ln e^* / \partial P)$ turns out to be determined by the difference between large and nearly equal quantities. Intuitively, one suspects that $(\partial \ln e^* / \partial P)_T$ should be negative -- the decrease resulting from increased electronic distortion as the solid is compressed.

Available $\omega_{TO}(P)$ data suggest that both positive and negative values of $(\partial\ln e*/\partial P)_T$ may be obtained, but in view of the poor accuracy of the data, positive values have to be viewed with caution.

More generally, pressure and temperature studies of phonon spectra of solid dielectrics are attracting more attention and much more work is needed in this important area in order to obtain quantitative estimates of anharmonic effects, as well as to shed some light on the origin of these effects. Understanding of lattice anharmonicities is important from the point of view of ferroelectricity since many ferroelectric transitions are believed to be driven by anharmonic effects. Such studies are also important from the standpoint of lattice stability and phase transformations since some transformations result from the instability of the crystal against a certain mode of vibration, i.e., the frequency of the mode becomes so low (with temperature or pressure) that the restoring force for the atomic displacements associated with the mode vanish and a transition sets in. Optical phonons can be studied by far IR absorption, Raman scattering, or inelastic neutron scattering; acoustic phonons can be studied by ultrasonic propagation, Brillouin scattering, or neutron scattering. The ultrasonic technique, which gives information about the long wavelength modes, has been very widely used to study the pressure dependence of the elastic properties (elastic constants) of solids and for high-pressure equation of state considerations.

Finally, measurements of ϵ_s provide an excellent and relatively simple probe for studying the detailed behavior and kinetics of phase transformations under pressure. Often apparatus design and other constraints limit the kind of probes available for such studies.

c. Ferroelectrics

Studies of the effects of pressure on ferroelectric (FE) crystals have shown that FE properties are among the most pressure (or volume) dependent of all physical properties. This is perhaps not too surprising since ferroelectricity is a structure-sensitive phenomenon and there is intimate coupling between the onset of FE ordering and lattice strain. Anharmonic interactions are of utmost importance in ferroelectricity, and, as pointed out earlier, pressure measurements are very useful for separating out anharmonic effects. Pressure studies can thus provide important information concerning the nature of of ferroelectricity, and in the case of some ferroelectrics such as KNO_3 and $LiH_3(SeO_3)_2$, such studies turn out to be essential for elucidating the FE behavior. In addition, as will be discussed later, pressure (or stress) effects on ferroelectrics have some direct practical applications.

The properties of a large number of FE crystals have been investigated under pressure. Recent reviews and assessments of the field are available in the literature.[10] It is difficult to draw general conclusions based on these investigations because of the varied natu of different classes of FE crystals (i.e., each crystal class exhibits a different mechanism for its ferroelectricity). Thus, the following remarks will be restricted to a few instances where pressure studies have led to significant advances in the basic and

phenomenological understanding of ferroelectricity -- under-
standing which has indirect practical implications and which
illustrates the importance of pressure as a variable in the
study of physical phenomena.

(1) <u>Soft Mode Ferroelectrics</u>: It is now established
that the dielectric properties and ferroelectric transi-
tion in some ferroelectrics, most notably the perovskites
such as $BaTiO_3$ and $PbTiO_3$, can be understood in terms of
soft optical phonons. The FE transition is caused by an
instability of the lattice against a long-wavelength trans-
verse-optic mode caused by the cancellation of the short-
range forces by the long-range Coulomb forces. Schematic-
ally the frequency of this mode is depicted by $\omega_{TO}^2 \propto$
(short-range forces) - (Coulomb forces). As $T \to T_0$,
the transition temperature, $\omega_{TO} \to 0$ and the static di-
electric constant, $\epsilon_s \to \infty$, ϵ_s and ω_{TO} being related by
a generalized LST relationship with the result that
$\epsilon_s \omega_{TO}^2$ = constant. The strong dependence of the proper-
ties on pressure can be qualitively appreciated by noting
that the short-range forces are much more strongly depen-
dent on interionic distance r than the Coulomb forces --
the latter vary as $1/r^3$ whereas the former vary more
like $\sim 1/r^{11}$. Thus the application of pressure causes
the short-range forces to increase much faster than the
Coulomb forces leading to an increase in the soft mode
frequency and a corresponding decrease in transition
temperature. It can also be readily appreciated that
the fractional increase in ω_{TO} with pressure becomes
larger as T approaches T_0, and this is reflected by the
fact that the Grüneisen parameter γ for this mode,

$\gamma \equiv -(\partial\ell n\omega_{TO}/\partial\ell nV)_T$, is found to increase very rapidly, reaching values of hundreds to thousands near T_O.

(2) <u>Antiferroelectrics</u>: Recent pressure studies have also played an important role in our present understanding of some antiferroelectric (AFE) crystals such as $PbZrO_3$. Because of the antiparallel nature of the displacements of similar ions in adjacent unit cells, the transition to an AFE state is associated with an instability of a lattice mode whose wavelength is of the order of a lattice parameter (i.e., a zone boundary mode). The experimental situation (at 1 bar) in $PbZrO_3$ and related AFE crystals suggested the presence of two, nearly "degenerate," low-frequency modes: a zone center TO (or FE) mode which is responsible for the large dielectric susceptibility and a zone boundary (AFE) mode which causes the transition. On lowering T at 1 bar, the crystal becomes unstable against the AFE mode just before the instability due to the FE mode is reached. While the validity of this description can in principle be checked by measuring the temperature dependence of the phonon dispersion curves by optical and neutron scattering techniques, such data are not available due to the lack of suitable single crystals. Recent dielectric constant pressure measurements on polycrystalline samples have, however, given the first experimental confirmation that the properties of these crystals are indeed determined by two separate modes. With increasing pressure the frequency of the FE mode increases (as discussed earlier) while that of the AFE mode decreases leading to a removal of the near "degeneracy" that exists between the two modes at 1 bar.

(3) <u>Hydrogen-Bonded Crystals</u>: Pressure studies have
proven to be important in the study of the FE and AFE
properties of hydrogen-bonded crystals of the KH_2PO_4-type.
The protons play crucial roles in the transitions in
these crystals as evidenced by the large changes in
transition temperatures and other properties observed
on replacing the protons by deuterons. It is now
believed that above the transition the protons exhibit
tunneling motion between two equilibrium positions along
the hydrogen bonds that connect adjacent PO_4 groups.
This motion is coupled to that of the other ions in the
crystal. The transition is triggered by the ordering
of the protons in their potential minima. The details
of the potential and thereby the tunneling frequency
are strong functions of the hydrogen bond length.
Pressure can be expected to strongly affect the transition
temperatures and properties of these crystals and this
is found to be the case. One of the most significant
findings is the recent observation of the vanishing of
the FE and AFE states at high pressures and 0° K in
KH_2PO_4 and $NH_4H_2PO_4$ at 17 and 33 kbar, respectively.[11]
This is believed to result from the increase in proton
tunneling frequency which causes the disordering ten-
dency of the tunneling field to be larger than the
ordering tendency of the dipolar field at all temperatures.

The possible vanishing of the FE state in other
classes of ferroelectrics has not been investigated
experimentally. It is expected, however, that this
will occur for soft TO mode ferroelectrics because of
the rapid increase of ω_{TO} with pressure. The manner
in which T_0 approaches 0° K at high pressure is par-

ticularly important from a theoretical point of view since it may help decide between competing models. For example in KH_2PO_4, $T_0 \to 0°$ with infinite slope, i.e., $dT_0/dP \to -\infty$, and this is consistent with the tunneling model.

(4) <u>Other Ferroelectrics</u>: Studies of $LiH_3(SeO_3)_2$ illustrate another aspect of high-pressure research. This crystal has by far the largest spontaneous polarization of any hydrogen-bonded ferroelectric, and it is unusual in that the forces responsible for the ordering of the dipoles are strong enough for the crystal to remain ferroelectric up to its melting point of 110° C. A ferroelectric-to-paraelectric transition can be (and has been) induced in this crystal only at high pressure. This results from the simultaneous increase in the melting point and decrease in the Curie point with increasing pressure. Thus, pressure studies made it possible to examine the details of the FE behavior at and near the transition, and these details provide important clues as to the nature of the ferroelectric ordering in this class of crystals.

KNO_3 is another interesting example in that its FE phase is thermodynamically stable only at high pressure. This phase can be obtained metastably at 1 bar over a very narrow temperature range of ~10° C. At high pressure the FE phase becomes stable over wide temperature ranges. It is quite likely that many of the high-pressure phases observed in a variety of dielectric crystals are ferroelectric; however, very little work has been done in this regard.

In view of ese examples, it can be seen that
high-pressure studies have provided important informa-
tion concerning the nature of ferroelectricity. For
perovskite- and KH_2PO_4-type ferroelectrics the pressure
results are in qualitative agreement with the accepted
model theories and, therefore, lend some support to
these models. Quantitative treatments are hampered by
the complicated nature of the phenomena and the fact
that the models have not been developed in sufficient
detail. Important theoretical questions remain un-
resolved and offer challenging problems. For example,
the exact origin of the temperature dependence of the
soft-mode frequency in the perovskites and the nature
of the proton-lattice coupling in the hydrogen-bonded
crystals are not clear. These are complex problems,
but they deserve additional investigation.

2. DIELECTRIC MATERIALS SYNTHESIS AND FABRICATION

a. Synthesis

The successful high-pressure synthesis of diamonds
in the late 1950's generated a great deal of research effort
in the United States, U. S. S. R., Japan, and other countries,
and there was high expectation that the high-pressure tech-
niques might lead to new and exotic dielectric materials for
a wide variety of applications. Unfortunately, with very few
exceptions (notably, diamond and cubic boron nitride which
are discussed elsewhere in this report), this expectation has
not materialized. Although a substantial number of new com-
pounds and new polymorphs have been prepared under pressure,
none of these has found practical applications and they remain
largely objects of academic interest. This is not to say,
however, that high-pressure synthesis is not a worthwhile

endeavor; rather, it is a specialized and expensive process that holds promise when used judiciously on sound scientific grounds.

The materials and processes listed below are some of those used in pressure synthesis of dielectric materials.[*]

(1) The syntheses of diamond and cubic boron nitride are by far the best and most important examples of high-pressure synthesis.

(2) Hydrothermal synthesis is of course a very widely used commercial process for producing such crystals as quartz and CrO_2, but the pressures here are very low -- up to a few thousand psi. There may be potential for extending the process to higher pressures, but the equipment becomes more involved and costly.

(3) The high-pressure synthesis of stishovite, the tetragonal rutile form of SiO_2, has been considered one of the important successes of Russian workers in this area. This material is of considerable geophysical and geochemical interest.

(4) There has been considerable expectation, largely on the part of Russian workers, for synthesizing new ferroelectrics of the ABO_3 type (e.g., perovskites) under pressure. This was motivated by ionic size considerations as discussed by Goodenough elsewhere in this report. A number of these oxides have been prepared under pressure

---

[*] The use of pressure in the chemical process industry (e.g., polyethylene) is extremely important but not considered here.

(e.g., $RbNbO_3$ and $RbTaO_3$), but at present none seems to have any especially attractive properties for practical applications.

(5)   A number of high-pressure phases can be retained metastably at 1 bar. Some examples include high-pressure modifications of SiO_2, ZnF_2, and TiO_2, the latter having been first recovered in shock-wave experiments. Many high-pressure phases can be easily retained by quenching to liquid nitrogen temperatures and retaining at low temperatures before releasing the pressure. One of the best examples is the metallic high-pressure phase of InSb. The technique allows one to study the properties of the high-pressure phase in much more detail than is possible at high pressure and is largely of scientific interest.

(6)   The apparent success in making diamonds on a commercial scale by shock-wave compression is an important achievement. The potential of the method for other syntheses is not known but it is most likely limited because of the unique nature and short duration (~ 1 μsec) of the compression.

(7)   High-pressure single-crystal growth is an area that has received little attention. The pressure range will be necessarily limited, but the process may have considerable potential in growing crystals of substances having high vapor pressure or in cases where pressure may suppress a phase transition which might interfere.

b.   Fabrication

High-pressure materials fabrication as referred
to here relates primarily to uniaxial and isostatic pressure
sintering. These are important, but mainly low-pressure
(< ~2 kbar) operations that are discussed elsewhere in the
report. Important examples of dielectric materials produced
this way are optical quality ceramics such as MgO, Y_2O_3 and
a family of lanthanum-doped lead zirconate-lead titanate
ferroelectrics.

The use of pressure in other fabrication areas
such as forming and hydrostatic extrusion of dielectrics will
not be discussed here.

3.   DEVICE APPLICATIONS

The large pressure-induced changes in dielectric
properties such as refractive index, optical absorption, con-
ductivity, static dielectric constant (capacitance), ferro-
electric polarization, phase transitions, etc., can in prin-
ciple be utilized in a variety of practical applications, much
in the same way as temperature-induced changes are utilized.
In practice, the requirements for a pressure generating system
make such applications unfeasible and/or impractical. However,
in a few instances this is not the case. These are either
such low-pressure (stress) applications so as not to present
any apparatus difficulties or very specialized applications.

In the realm of low pressures (or more properly
low stresses) there are a wide variety of strain and stress-
biased devices and electromechanical transducers, many using
piezoelectrics such as quartz and ferroelectric ceramics.
The most recent application involves the use of strain to

cause a change in the birefringence of optical quality ceramics for electro-optic image storage and display. In all of these applications the stresses are so low that they are outside the scope of our immediate concern.

In the area of high pressures there are a few unique and important applications of dielectric phenomena which are worth mentioning. Most of these involve shock-wave compression. Areas of additional needed research are mentioned.

a. Piezoelectric Shock-Wave Stress Gages

These gages yield stress-time records of shock-wave events with submicrosecond resolution.[12] The application of stress produces a change in polarization of the piezoelectric material and this in turn causes an electrical current to flow in a low impedance external circuit. The current is proportional to the stress. The amplitude and time dependence of this current are functions of the piezo-electric and dielectric constants and the mechanical proper-ties of the material under shock-loading conditions. The gages operate in the elastic compression range, and fortunately there are a number of piezoelectric materials, such as quartz, lithium niobate, and lead zirconate-lead titanate ceramics, which have rather high Hugoniot elastic limits and make it possible to use such gages over a wide range of pressure. Quartz is by far the most widely used piezoelectric for this applica-tion. It remains elastic up to ~ 60 kbar under shock con-ditions. Its piezoelectric, dielectric, and mechanical properties under shock have been investigated in some detail. Similar knowledge of the properties of other piezoelectrics is rather limited and much more work is needed in this specialized but important area.

The application of very high stress to a strongly
piezoelectric material produces very high electric fields
within the material. In quartz these fields can be and
often are in the 10^5-to 10^6- volt/cm range. Such high fields
can cause conduction or severe dielectric breakdown which
interfere with the normal operation of the gage. Evidence
for conduction and breakdown has been observed under certain
conditions in quartz gages and these conditions have been
experimentally defined. Again similar data are lacking for
other piezoelectrics. In all cases the mechanism for the
electrical conduction and the nature of the breakdown under
the dynamic conditions in question are not understood and
represent areas sorely in need of more research. The more
general problem of dielectric breakdown in shock-wave environ-
ments often causes experimental and systems failure and is a
matter of serious concern. Dielectric breakdown under normal
conditions is poorly understood and much less is known about
the problem under shock. Studies of dielectric strength at
high static pressures might be helpful, but these will not
serve as a substitute for the dynamic case.

b. Capacitive Shock-Wave Stress Gages

The operation of such gages is based on the change
in the capacitance of a solid dielectric disc resulting from
the changes in the static dielectric constant and thickness
produced by the application of shock pressure. A gage of
this type utilizing sapphire discs has been used successfully.[13]
It is capable of measuring stress-time profiles with resolution
limited only by the rise-time of the recording equipment and
the planarity of the shock-wave front. The change in capac-
itance of the electroded disc, across which an electrostatic

potential is applied, causes a current to flow in a low
impedance circuit. The current is instantaneously (very
small circuit time constant) proportional to the particle
velocity at the stressed electrode.

Sapphire is well suited for this application because
it behaves elastically to large compressions. Its Hugoniot
elastic limits along different crystallographic orientations
are unusually high, varying from 120 to 200 kbar. However,
the change in the dielectric constant of sapphire with stress
is very small and large potential differences of the order of
kilovolts have to be applied across the disc to produce use-
ful currents especially at low stress. It would be desirable
to find other suitable dielectrics with larger pressure-
induced changes in dielectric constant for this application.

c. Power Sources

Some unique power sources, capable of delivering
large electrical voltage or current pulses to a load, can
be made. These are one-shot devices that operate on the
basis of the charge released from a polarized ferroelectric
disc by the application of shock compression. The amount of
charge release or depoling depends on the stress, and above
a certain stress complete depolarization may occur. This
would correspond to a transition from the ferroelectric to
the paraelectric phase. In its ferroelectric phase a ferro-
electric material is also strongly piezoelectric and the
application of shock stress causes rather complicated non-
linear electromechanical effects. More work is needed in
order to quantitatively understand these effects.

Strongly piezoelectric (but nonferroelectric) di-
electrics such as quartz can also be used for such power
sources. For example, quartz discs are capable of producing
kilovolt pulses.

d. Other Electrical Pulses

Useful current and voltage pulses have been obtained
from a variety of dielectrics exposed to shock-wave loading.
For example, very thin (~ 0.005-cm thick) anodized aluminum
layers produce a voltage that increases with stress and
amounts to more than 1 volt/kbar up to 100 kbar.[14] Thin
layers of plastic tape produce tens of volts.[15] Such effects
have been successfully used as inexpensive methods for detect-
ing the arrival of shock waves at surfaces.

Electrical signals from other shock-loaded di-
electrics, especially ionic crystals such as the alkali
halides, have been observed and some speculative explanations
based on the generation and motion of dislocations given. In
general, all of these phenomena are poorly understood, and
more work is needed in this area.

REFERENCES

1. J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev., 92, 890 (1953).

2. J. Pirenne and E. Kartheuser, Physica, 30, 2005 (1964).

3. R. S. Krishnan, Progress in Crystal Physics, Vol I (S. Viswanathan, Madras, India) 1958.

4. See e.g., the extensive pressure work of K. Vedam and co-workers: Phys. Rev., 146, 548 (1966); Sol. State Comm., 3, 573 (1965); Matl. Res. Bull., 4, 573 (1969); Phys. Rev., 181, 1196 (1969).

5. B. Szigeti, Trans. Farad. Soc., 45, 155 (1949); Proc. Roy. Soc., (London) A204, 51 (1950); A252, 217 (1959); A261, 274 (1961).

6. A. J. Bosman and E. E. Havinga, Phys. Rev., 129, 1593 (1963); 140, A292 (1965).

7. G. A. Samara, Phys. Rev., 165, 959 (1967); Solid State Comm., 4, 279 (1966).

8. R. P. Lowndes and D. H. Martin, Proc. Roy. Soc., (London) A308, 473 (1969); A316, 351 (1970).

9. See e.g., S. S. Mitra et al., Phys. Rev. Letters, 18, 455 (1967); Phys. Rev., 174, 983 (1968).

10. G. A. Samara, in "Advances in High Pressure Research," edited by R. S. Bradley (Academic Press, New York, 1969) Vol. 3, Chapt. 3. See also G. A. Samara and H. G. Drickamer, Comments on Solid State Physics, 3, 1 (1970).

11. G. A. Samara, Phys. Rev. Letters, 27, 103 (1971).

12. R. A. Graham, F. W. Neilson, and W. B. Benedick, J. Appl. Phys., 36, 1775 (1965). See also J. Appl. Phys., 43, 826 (1972).

13. R. A. Graham and G. E. Ingram in "Behavior of Dense Media Under High Dynamic Pressures," Gordon and Breach, New York 1968.

14. A. R. Champion, _J. Appl. Phys._, 40, 3766 (1969).

15. A. R. Champion and W. B. Benedick, _Rev. Sci. Instr._, 39, 377 (1968).

APPENDIX J

HIGH-PRESSURE TECHNOLOGY AND MAGNETISM

by John B. Goodenough

Lincoln Laboratory, Massachusetts Institute of Technology

Lexington, Massachusetts

1. MOTIVATIONS

High-pressure technology provides an additional physical variable that is useful in three primary areas: (a) devices, (b) materials preparation and processing, and (c) exploration of physical phenomena.

To date, relatively little attention has been given to the use of high pressures in devices. This is primarily due to the stationary, expensive character of most high-pressure installations. However, mobile units of quite compact size have been built. At Lincoln Laboratory, there is a mobile "hydrostatic"-pressure unit capable of 14-kbar pressure over a temperature range from 1.5 to 1000° K. Such a unit can be brought to different measurement stations in the laboratory, thus greatly enhancing the range of investigations that are readily accessible to high pressure as a variable. Once relatively inexpensive, mobile pressure units become available, their use as control elements becomes feasible. For example, the energy gap between the valence and conduction bands of a diode laser can be significantly modulated by high pressure, so that pressure provides a control of the laser frequency. A modification of the Lincoln Laboratory mobile pressure unit is now being constructed to provide a tunable diode laser.

Uniaxial (tensile or compressive) stress may also provide an important control variable. For example, the simple strain gauge, which monitors electrical resistance as a function of tensile strain, provides a sensitive sensor. Uniaxial stress on a magnetostrictive ferromagnet can completely alter its permeability, or the shape of its $B-\mu_{o}H$ hysteresis loop and a modest uniaxial stress on a metamagnetic material may change an antiferromagnetic-to-ferromagnetic transition temperature by tens of degrees centigrade. Although such phenomena have not been exploited by present technology, they may prove important in the future.

The preparation of optical-quality ceramics by hot-pressing techniques is of particular interest for transparent dielectrics useful for light modulation. However, magnetic properties are also sensitive to pores and grain boundaries. Furthermore, control of a transition-metal valence state often required a low-temperature preparation that may only be possible under high pressures. Therefore high pressure is an important processing variable in the preparation of dense magnetic ceramics by solid-state reactions at relatively low temperatures.

High pressure as a thermodynamic variable enlarges the range of compounds and structures practically available to synthesis. This enlargement manifests itself in four ways: (a) new compounds, such as ferromagnetic CrO_2; (b) new polymorphs metastable at ambient temperature, such as diamond or ferrimagnetic $CsNiF_3$; (c) phases with smaller numbers of native defects, such as superconducting TiO

and a stoichiometric FeO; and (d) easier synthesis of compounds
marginally accessible by preparation at atmospheric pressure.
(Illustrative examples may be found elsewhere;[1,2] a few are
presented later in this appendix.)

Many solid-state phenomena have been explored with
high pressure as a physical variable. Of particular interest
is the variation with lattice parameter of the various phenom-
enological constants directly accessible to measurement. These
constants are interrelated by microscopic solid-state theory.
Therefore, their relative variation with pressure provides an
important test of existing theory as well as a demonstration
of pressure sensitivities that may have technological signifi-
cance.

Generally, but not always, the easiest phenomena to
monitor are phase transformations. Magnetic phase transforma-
tions occur at critical temperatures and at critical volumes.
Changes in only magnetic order occur at critical temperatures
that vary with volume, and changes in the magnitudes of ordered
atomic moments occur at critical volumes that may have little
temperature dependence. Transitions involving changes in the
magnitudes of disordered atomic moments may be first-order,
occurring at well-defined transition temperatures, or they
may be higher-order. Such transitions are to be distinguished
from changes with temperature in the relative populations of
ground and excited states of localized-electron f^n or d^n
manifolds having the same n, but different net atomic moments.
Changes in magnetic transition temperatures with pressure are
commonly obtained by monitoring electrical resistivity or
inductance. However, DTA, neutron-diffraction, Mössbauer,

and/or x-ray measurements under pressure may be necessary
supplements to a meaningful interpretation of the data.

Measurements of atomic moments and magnetic aniso-
tropy may be obtained from magnetometer measurements. The
most versatile instrument for this purpose, developed at
Lincoln Laboratory, is the vibrating-coil magnetometer that
permits continuous monitoring of sample magnetization as a
function of applied magnetic field, temperature, and pressure.
The Japanese have used portable pressure bombs in conjunction
with a pendulum magnetometer, but this method does not provide
simultaneous monitoring of the pressure and the magnetization.
Magnetometer measurements with pressure have one important
advantage over electrical measurements: there are no electrical
leads, and measurements on polycrystalline samples are in-
dependent of any cracking of the specimen with pressure.

Problems of particular interest for magnetism
include: (a) shifting with pressure of a conduction-band
edge relative to a donor level or a valence-band edge; (b)
critical lattice parameters for strong vs weak electron
correlations; (c) variations with pressure of charge-transfer
exchange processes, which are responsible for couplings
between excited states in optical devices as well as for the
couplings between ground states that are responsible for any
long-range magnetic order; and (d) exploration of temperature-
bandwidth phase diagrams, the bandwidth of allowed energies
for magnetic electrons being sensitive to pressure. Closely
related to this latter problem is the use of pressure to
distinguish between the influence of chemistry and of lattice
parameter on the physical properties of alloys and mixed
systems.

2. SOME ILLUSTRATIVE EXAMPLES

a. New Compounds

(1) CrO_2

Where chemical reaction does not take place at atmospheric pressure, high pressure may induce synthesis by lowering the free energy of the compound relative to that of the components. It is useful to identify those cases where this situation may occur. A rather interesting case appears to apply to the stabilization of octahedral-site Cr^{4+} ions in oxides.

Outer d electrons at transition-metal cations may be either localized or itinerant, depending upon the magnitude of the coupling energy between d electrons on neighboring cations. Where the coupling is of intermediate strength, the d electrons are relatively unstable. Application of pressure enhances the interactions between d electrons on neighboring atoms; therefore, it increases any itinerant-electron bandwidth. If only bonding d orbitals are occupied, increasing the d-electron bandwidth stabilizes the phase, and the increase in stabilization with pressure is particularly sensitive where the d bands are very narrow at atmospheric pressure. The $Cr^{4+}-O^{2-}-Cr^{4+}$ interactions via the $2p_\pi$ orbitals on the anions are of intermediate strength in the perovskites $A^{2+}CrO_3$ -- $SrCrO_3$ is metallic and Pauli paramagnetic whereas $CaCrO_3$ and $PbCrO_3$ are spontaneously anti-ferromagnetic and exhibit Curie-Weiss paramagnetic

susceptibilities -- and in the ferromagnetic metal CrO_2. These compounds have only been synthesized under pressure. Hydrothermal synthesis is used to prepare CrO_2 for high-quality magnetic recording.

(2) $RbNbO_3$

Many oxides, fluorides, and chlorides of chemical formula ABX_3 crystallize in one of the hexagonal-perovskite polytypes.[1,3] These structures consist of ordered, close-packed AX_3 layers stacked in cubic or hexagonal or mixed cubic and hexagonal stacking sequences. The smaller B cations occupy all the interlayer X-anion octahedral interstices, and stabilization of these structures requires not only that the larger A cation have a radius $r_A >0.9Å$, but also that the B cation be stable in an octahedral interstice.

If the stacking of AX_3 layers is entirely cubic, the B-cation octahedra share only corners to form the 3C structure of cubic perovskites. In this structure the A cations are confined to a cubic cage of edge B-X-B, where the B-X bond length is a characteristic of the B and X ions that requires considerable energy to increase. This cage creates an upper limit on the A-cation size that can be accommodated in a given BX_3 cubic array. Such geometrical reasoning gives the Goldschmidt tolerance factor

$$t = (r_A + r_X) / \sqrt{2}(r_B + r_X) \qquad (1)$$

and the ideal cubic structure is anticipated for

$t = 1.0$. In fact, the cubic perovskite structure is found over a range

$$t_\ell < t < t_u \tag{2}$$

where the upper limit is anticipated to fall close to $t_u = 1.0$. For smaller values of t, distortions from cubic to rhombohedral or orthorhombic symmetry optimize the A-X bonding at lower temperatures.

If the stacking of AX_3 layers is entirely hexagonal, the B-cation octahedra form face-shared linear chains parallel to the c-axis of the hexagonal (2H) cell. Since these chains are isolated from one another, relatively large A cations can be accommodated by adjustment of the c/a ratio. Therefore, this hexagonal perovskite structure is competitive where t> 1, as t becomes larger. However, accommodation of the larger A cation is at the expense of considerable Madelung energy, a large electrostatic repulsive force occurring between B cations in face-shared octahedra.

In a narrow, intermediate range of t, three intermediate stacking sequences have been identified: two-to-one cubic to hexagonal stacking (cchcch of the 6H structure), a one-to-one stacking (chch of the 4H structure), and a one-to-two stacking chhchhchh of the 9R structure). In these intermediates, the loss of Madelung energy is reduced by displacing oppositely along the c axis the B cations in face-shared octahedra. However, chang-

ing the stacking sequence also requires energy,
so that the 4H polytype is only found in oxides.
In fluorides, where the Madelung energy is relative-
ly small, the various polytypes occur in definite
ranges of t:

Orthorhombic distortion of 3C $0.78 < t \leqslant 0.88$
     ($GdFeO_3$-type)

Cubic 3C $0.88 \leqslant t \leqslant 1.0$

Hexagonal 6H (Hex. $BaTiO_3$-type) $1.0 < t \leqslant 1.06$

Rhombohedral 9R ($CsCoF_3$-type) $t = 1.07$

Hexagonal 2H ($CsNiF_3$-type) $t \geqslant 1.08$

In oxides, both t_u and the ranges of t over which
the given polytypes are stable depend upon the
effective charges of the B cations. Nevertheless,
pressure always stabilizes cubic relative to
hexagonal stacking.

Stoichiometric $BaTiO_3$ has the 3C structure,
even though t = 1.06. At lower temperatures it
exhibits ferroelectric distortions having techno-
logical importance. In these distortions, the
Ti^{4+} ions are displaced cooperatively from the
center of symmetry of their interstices to form
one, two, or three shortest Ti - O bonds. The fact
that $CaTiO_3$ (t<1.0) undergoes no ferroelectric
distortion has suggested that the ferroelectricity
of $BaTiO_3$ is due to a stretching of the Ti - O
bond by a t> 1.0. Furthermore, a 3C polytype
having t = 1.06 is stabilized because the large
effective charge on the Ti^{4+} ion inhibits the
formation of a face-shared octahedra.

This reasoning suggested that $RbNbO_3$ and $RbTaO_3$, which have t = 1.08, cannot be synthesized at atmospheric pressure because the large B-cation charge prohibits the formation of hexagonal polytypes and the large A-cation size inhibits formation of the 3C structure. However, it followed that their synthesis should be accessible under pressure, and $RbNbO_3$ was prepared at 65 kbar and 900° C, $RbTaO_3$ at 90 kbar and 900° C. Whereas $RbNbO_3$ exhibits the ferroelectric distortions of $BaTiO_3$ at atmospheric pressure, $RbTaO_3$ remains cubic. This information indicates that not only stretching of the B - O bonds, but also a small octahedral vs. tetrahedral site-preference energy are required for a ferroelectric displacement of the B cations.

b. New Polymorphs

From the above discussion, it is apparent that ABX_3 polytypes having a larger fraction of cubic stacking can be prepared at high pressures. In the case of oxides and fluorides, these high-pressure structures are metastable at atmospheric pressure to high (T ~ 1000° C) temperatures. The high-pressure formation of polytypes having a greater fraction of cubic stacking is a general phenomenon and has been extensively studied in the rare-earth metals.

A ferrimagnetic material that is transparent in the visible and in the IR out beyond 10μm would be technologically important, especially where the Curie temperature is above room temperature. At atmospheric pressure, $RbNiF_3$ forms in the 6H structure and is ferrimagnetic below $T_c = 139°$ K. Although transparent in the near IR, lattice absorption begins to be

intolerable at 7μm. In order to push the absorption edge
out to longer wave lengths, it is necessary to have a compound
containing heavier ions. Although $CsNiF_3$ crystallizes in the
hexagonal 2H polytype, a metastable 6H structure can be formed
at P = 60 kbar. This phase is also ferrimagnetic with a $T_c \approx$
111°K and an IR cut-off beginning at 9μm. To extend the limit
beyond 10μm, it appears necessary to go to heavier anions.
Unfortunately the ferrimagnetic $ABC\ell_3$ compounds are unstable
at room temperature. Nevertheless, this example illustrates
how high pressure may be useful for the synthesis of a meta-
stable polymorph, other than diamond, of technological impor-
tance.

c. Reduction of Native Defects

The preparation of wide-gap semiconductors for effi-
cient light-emitting diodes or for diode lasers at visible
frequencies has proven an illusive goal. The principal reason
is the existence of native defects that prevent the preparation
of both n-type and p-type semiconductors of the same wide-gap
material. Evidence that this situation might be alleviated
by high-pressure synthesis comes from successful improvement
of the stoichiometry in several transition-metal oxides.

Antiferromagnetic FeO_{1+x} is oxygen-rich if prepared
at atmospheric pressure. However, the high-pressure prepara-
tion of stoichiometric FeO has recently been reported. Simi-
larly, $A^{2+}FeO_{3-x}$ is always oxygen-poor if prepared at atmo-
spheric pressure, but synthesis under high oxygen pressure
yields stoichiometric compounds. A high oxygen pressure can
be obtained with a double cell having CrO_3 in one chamber
and the sample in the other chamber.

Superconducting TiO contains about 16% cation and anion vacancies that order below 900° C. These vacancies may be at least partially removed by high-pressure synthesis.

d. Easier Synthesis

Many solid-state reactions are extremely slow or lead to poorly crystallized products if carried out at atmospheric pressure. Where the product is stabilized by pressure, high pressures may reduce reaction times to less than an hour and/or markedly increase the crystallinity of the product. For example, synthesis of the orthoferrites $LnFeO_3$ by normal ceramic techniques usually requires several days of regrinding and firing, whereas they may be prepared in half an hour at 50 kbar and 1200° C.

Although $NaSbO_3$ and $KSbO_3$ have a tolerance factor t compatible with the formation of a perovskite structure, these compounds crystallize in the ilmenite structure at atmospheric pressure. However, $KSbO_3$ transforms to a cubic structure -- space group Pn3 -- if annealed at 1000° C for several weeks. Treatment of the ilmenite phase for only 5 minutes at 800° C and 20 kbar is sufficient to transform it to a disordered, cubic I23 structure. The Pn3 and I23 structures each have the same $(SbO_3)^-$ array, which contains tunnels along the body diagonals. The difference between the structures is due to ordered vs disordered arrangements of the alkali atoms in the tunnels. Given $KSbO_3$ in the I23 structure, it is possible to prepare $NaSbO_3$, $LiSbO_3$, and $AgSbO_3$ compounds with the same $(SbO_3)^-$ array by ion exchange. Such tunnel structures may be useful as solid-state electrolytes.

e. Shifting a Band Edge

The ferromagnetic compound EuO may be made either europium-rich or europium-poor. The stoichiometric compound is an insulator having a $4f^7$ localized-electron manifold near the bottom of a large energy gap between the $O^{2-}:2p$ valence and $Eu^{2+}:5d$ conduction bands. If the compound is europium-rich, anion vacancies serve as electron traps for the excess electrons, and above the Curie temperature EuO_{1-x} is an n-type semiconductor. The trap, or donor, states appear to have energies that are relatively independent of the position of the 5d band edge, and below the Curie temperature $T_c \approx 70°K$ the edge of the parallel-spin 5d band is stabilized by the Weiss molecular fields to below the trap level. Therefore a metal-to-semiconductor transition occurs near the ferromagnetic Curie temperature. An alternate method of changing the relative position of the 5d band edge is high pressure, which broadens the 5d band. Monitoring the change in resistivity and in optical absorption edge with pressure at room temperature provided an excellent test of the model.

In the case of SmS, a localized $4f^6$ level lies just below the 5d band edge, and 6.5 kbar causes sufficient broadening of the 5d bands to induce a first-order volume reduction due to $4f^6 \rightarrow 4f^5 5d^1$ electron transfer at each samarium atom. The device potential of such a phenomenon has yet to be explored.

f. Critical Atomic Volumes

The d electrons of neighboring transition-metal atoms may interact directly (M-M interactions) or via an intermediary anion (M-X-M interactions). In either case,

reduction of the atomic volume enhances the strength of the interaction. Three critical volumes are of fundamental interest: (1) that at which the pressure dependence of the magnetic-ordering temperature changes sign, (2) that at which spontaneous magnetism disappears, and (3) that at which there are abrupt changes in the magnitude of the atomic moments.

To date, there are no known examples where a change in sign of $\partial T_c/\partial P$ has been observed. This fact is, in itself, informative since it suggests two distinguishable thermodynamic states for the outer d electrons. Transitions from a semi-conducting, spontaneously antiferromagnetic phase to a metallic, Pauli paramagnetic phase have been observed in several com-pounds. Metastable, hexagonal NiS, for example, exhibits a first-order semimetal-to-metal phase change at an antiferro-magnetic Néel temperature T_N, and the antiferromagnetic phase can be completely quenched by hydrostatic pressures P>20 kbar. There appears to be no symmetry change across this transition. The compound MnAs exhibits a first-order change in the mag-nitude of its atomic moment at the Curie temperature. Experi-ments with hydrostatic pressure on this compound and on the systems $MnAs_{1-x}P_x$, $MnAs_{1-x}Sb_x$ have established that there is a sharp change in the magnitude of the intra-atomic exchange energy at a critical atomic volume. The system $V_{2-x}Cr_xO_3$ has a low-temperature, anti-ferromagnetic phase that can be quenched by high pressure (P>26 kbar for V_2O_3). For small x, it also has a high-temperature metal-to-semiconductor transition that reflects changes in electron correlations as well as shifting band populations. There are several interesting features of this system that have important theoretical implications, including evidence of a critical

lattice parameter in the basal plane, and hence a critical bandwidth, for the support of spontaneous magnetism.

g. Exchange Processes

The most straightforward way to investigate the sensitivity of interatomic-exchange couplings to the lattice parameters is to monitor changes in magnetic order, magnetic-ordering temperatures, and the paramagnetic Weiss constant as a function of pressure. The sign of $\partial T_c/\partial P$ may reflect competing exchange interactions, but where these complications are missing it provides an interesting criterion for distinguishing localized from itinerant electrons. Measurements of $\partial T_c/\partial P$ for several itinerant-electron ferromagnets have provided important checks on the Stoner theory of ferromagnetism. Neutron-diffraction measurements of elemental chromium under hydrostatic pressure have provided constraining data for any theory of the spin-density waves in this itinerant-electron antiferromagnet. In particular, any theory of the spin flip relative to the propagation direction of the spin-density wave must also account for the pressure dependence of this phenomenon. In the system $Mn_{2-x}Cr_xSb$, an exchange-inversion temperature is found in a small interval of x. This appears to be intimately associated with the atomic volume and could profitably be investigated as a function of pressure.

h. Chemical vs Volume Effects

Investigations of the temperature dependence of magnetic properties as a function of magnetic-electron bandwidth must make use of chemical substitutions as well as of pressure. However, chemical substitutions require one to distinguish between the influence of chemical and of volume changes. In

the perovskite system $Ca_{1-x}Sr_xMnO_3$, for example, the Néel temperature increases with x, or $\partial T_N/\partial a_0 > 0$, whereas a $\partial T_N/\partial P > 0$ indicates just the opposite dependence on cell size. A distortion of the perovskite to orthorhombic symmetry gives rise to a weak ferromagnetism due to a canting of the antiferromagnetically coupled spins. The cant angle, and hence the magnetization σ_0, varies with the magnitude of the distortion. Therefore, by monitoring both $\partial T_N/\partial P$ and $\partial \sigma_0/\partial P$ for different values of x, it was possible to show that $\partial T_N/\partial x > 0$ is due to chemical rather than geometrical effects. This finding has important implications for any interpretation of the variations in magnetic properties found among the transition-metal oxides having the perovskite structure.[3]

3. FINAL REMARKS

No attempt has been made here to summarize the considerable amount of work that has been done on the preparation of magnetic materials and the investigation of their properties under hydrostatic or uniaxial stress. Rather, emphasis has been given to the principal motivations for use of high-pressure techniques in this field, and the few illustrative examples have been chosen to indicate how this tool is being used in exploratory research. Only oblique references are given to the technique's potential impact on technology. It seems clear, however, that a properly orchestrated effort could sharply enhance the influence of high-pressure technology on all three aspects of the materials field: devices, materials preparation and processing, and understanding and control of physical phenomena. However, proper orchestration would make high-pressure technology a tool within a larger materials effort rather than an end in itself.

The experimentalist responsible for the high-pressure
apparatus and measurements at Lincoln Laboratory is James A.
Kafalas. The vibrating-coil magnetometer was developed by
Kirby Dwight and Norman Menyuk after an early design by
Donald O. Smith.

4. RECOMMENDATIONS

The topics covered in this presentation may be related
to the stated DoD pacing material problem areas as follows:

a. Pressure as a Variable (Evaluation of Pressure
   Effects on....)

   (1) Diode lasers: -- tuning

   (2) Electro-optic materials: -- pressure-induced
       metal-insulator transition introduces a
       mirror-to-window transition in the near IR.
       Examples: SmS, $(V_{1-x}Cr_x)_2O_3$

   (3) Magnetic materials: -- (a) permeability changes
       induced by tensile stress, as in Permalloy,
       and (b) pressure-induced magnetic transitions,
       as in MnAs.

   (4) Dielectric materials: -- pressure modulation
       of the dielectric constant in the vicinity of
       a ferroelectric Curie temperature.

b. Materials Processing

   (1) Vacuum hot pressing: -- (i) Removal of pores
       from sintered specimens may yield (a) optical-
       quality, polycrystalline windows of greater
       mechanical strength than single crystals, (b)
       optical-quality Faraday rotators, and (c)
       higher magnetic permeabilities in ferrite
       materials.

      (ii)   Sintering at lower temperatures helps to control cation valence and hence to reduce dielectric loss.

(2) High-pressure preparation:

      (i) Reduction of atomic vacancies as demonstrated in TiO and SnTe (tin vacancies reduced by a factor of five) improves stoichiometry and may permit the fabrication of p-n junctions in wide-gap semiconductors for LED and diode (tunable) lasers in the visible.

      (ii) Reduction of sintering temperatures offers control of cation valence and hence reduction of dielectric losses.

     (iii) Extrusion: -- fabrication of polycrystalline rods and plates.

c.   Synthesis (Search for New Supermaterials)

It is generally possible to extrapolate from known materials to the design of unknown materials that would improve a desired physical property. It is also possible, in general, to determine whether pressure is a variable that makes synthesis of the unknown material more or less probable. The following examples (see 2. (a)) are illustrative:

(1) New compounds: -- CrO_2 is a hard magnet that can only be prepared at pressure (hydrothermal synthesis is used industrially) and that gives magnetic tapes of higher performance.

(2) New polymorphs: -- The 6H form of $CsNiF_3$ is an example of a new ferrimagnetic material transparent to optical and IR frequencies, and $NaSbO_3$ having the cubic structure of $KSbO_3$ is a new solid-state electrolyte of considerable promise as a higher efficiency electrolytic power source material.

(3) Easier synthesis: -- The orthoferrites $LnFeO_3$ exhibit a weak ferromagnetism that is of potential interest for "bubble-domain" devices. Preparation of sintered samples is greatly facilitated by high pressure. High pressure might also aid single-crystal preparations.

2. Comments

(1) There is a clear need to develop techniques other than hydrothermal synthesis for the growth of single crystals at high pressures.

(2) High-field superconductors and compounds exhibiting some types of metal-insulator transition generally have structures that tend to be unstable. If metastable phases can be prepared, these may exhibit interesting transitions at lower temperatures. For example, the stable low-temperature form of NiS is millerite, but quenching from 900° C retains the hexagonal $B8_1$ structure, which is metastable below 300° C. This metastable phase undergoes a first-order isosymmetric transition below room temperature from an antiferromagnetic semimetal

at $T < T_N$ to a Pauli paramagnetic metal at $T > T_N$.
Since many high-pressure phases are metastable
at atmospheric pressure, new metastable compounds
with exploitable properties may be discovered with
high-pressure techniques.

REFERENCES

1. J. B. Goodenough, J. A. Kafalas, and J. M. Longo, "High-Pressure Synthesis" in "Preparative Methods in Solid State Chemistry," P. Hagenmuller, ed., (Academic Press, New York, 1972, pp. 1-69).

2. D. B. McWhan, "The Pressure Variable in Materials Research," Science, 176, 4036 (1972).

3. J. B. Goodenough and J. M. Longo, "Landolt-Bornstein Tabellen, Neue Serie," Vol. III/4a. pp. 126-314 (Springer-Verlag, Berlin, 1970).

BIBLIOGRAPHY OF
PUBLISHED REVIEW ARTICLES ON HIGH PRESSURE

ELECTRICAL PROPERTIES: H. G. Drickamer, G. K. Lewis, Jr., and S. C. Fong, Science, 163, 885 (1969); H. G. Drickamer, Science 156, 1183 (1967) and 142, 1429 (1963).

SEMICONDUCTORS: W. Paul and D. M. Warschauer in "Solids Under Pressure," (McGraw-Hill Book Co., New York, 1963).

SUPERCONDUCTIVITY: R. I. Boughton, J. L. Olsen, and C. Palmy, Progr. Low Temp. Phys., Vol. VI, C. J. Gorter, ed. (North Holland) p. 169; N. R. Brandt and N. I. Ginzburg, Scientific Amer., 224, 83 (1971) and Usp. Fiz. Nauk, 98, 95 (1969) [Sov. Phys. USPEKII, 12, 344 (1969)].

MAGNETISM: D. Bloch and A. S. Pavlovic, <u>Adv. High Pressure Research 3</u>, R. S. Bradley, ed. (Academic Press) p. 41; D. Bloch, <u>High Temp.-High Pressures</u>, 1, 1 (1969).

FERROELECTRICITY: G. A. Samara, <u>Adv. High Pressure Res.</u>, Vol. 3, R. S. Bradley, ed. (Academic Press, 1969) p. 155.

GEOPHYSICS: F. R. Boyd, <u>Science</u>,145, 13 (1964); R. C. Newton, <u>Adv. High Pressure Res.</u>, 1, R. S. Bradley, ed. (Academic Press, 1966) p. 195.

CHEMISTRY: E. Whalley, <u>Annual Reviews of Physical Chemistry</u>, 18, 205 (1967).

STRUCTURE: "Proceedings of Symposium on X-ray Diffraction at High Pressure," D. B. McWhan, ed., <u>Trans. Amer. Cryst.Assoc.</u>, 5 (1969); M. D. Banus, <u>High Temp.-High Pressure</u>, 1, 483 (1969); W. Klement, Jr. and A. Jayaraman, <u>Prog. Solid State Chem.</u>, 3, 289 (1966).

APPENDIX K

VERY HIGH PRESSURES USED IN POLYMER TECHNOLOGY

by W. P. Slichter
Bell Laboratories
Murray Hill, N. J.

This survey omits the important use of elevated pressures in the synthesis of high polymers. As in areas of chemistry that pertain to organic and inorganic chemistry, so also is the use of high pressure an important variable in synthetic processes.

The exploitation of elevated pressures has great potential in adding to an understanding of polymeric substances. This statement can equally be made with respect to virtually the entire catalog of useful compounds; indeed, there are many examples of technological studies that have hinged upon information derived from the pressure dependence of key parameters. With polymers, regrettably, this information is still sparse. The relative complexity of these materials, both in structure and in thermodynamic state, makes them unattractive as candidates for investigation at elevated pressure. This situation is unfortunate, for this very complexity requires the use of every powerful variable to clarify the fundamental properties and behavior of the substances.

High polymers occur in technology either as partly crystalline substances or as wholly amorphous materials. Fully crystalline polymers are experimentally contrived oddities of some theoretical interest. No meaningful studies

of the use of elevated pressure on these materials have
been reported. On the other hand, partly crystalline and
wholly amorphous polymers comprise all the polymers of tech-
nological importance. The properties of these materials are
strongly influenced by pressure.

We identify three categories of structural organi-
zation for bulk polymers: (1) crystalline regions; (2) rub-
bery structures; (3) glassy arrays. Depending upon the mole-
cular character of the compound, the temperature, and the
pressure, transformation from one to another of these orga-
nizations can be effected on a given time scale. We speak
of two characteristic temperatures: (1) the melting point
(T_m), and (2) the glass temperature (T_g). In contrast to
the behavior of compounds of low molecular weight, T_m is
affected by many variables (e.g., molecular weight, time
scale, pressure). Similarly, T_g is also pressure-dependent.

In the case of T_m, the pressure dependence is evi-
dently related to variations in the morphology. Information
is largely confined to the behavior of polyethylene. This
partly-crystalline polymer has been shown by Geil, Wunderlich,
and others to have a lamellar crystalline structure that
depends on pressure. In studies by electron microscopy, it
is found that moderately high pressures during crystalliza-
tion from the melt (e.g., pressures in the range 10^4 atmos-
pheres and higher) lead to morphologies in which the crys-
talline lamellae consist of folded chains, with a fold
length of ~ 100 Å. The technological value, if any, of these
high-pressure forms of polyethylene (and other polymers yet
to be studied) is still unknown, since current techniques of
extrusion and molding occur at pressures well below this

range of unusual behavior. Certainly there is fundamental
information to be gathered with respect to the kinetics and
thermodynamics of crystallization in polymers, but it is not
yet known if there is also technological promise.

The variability of T_g with pressure is known both
for polymeric and monomeric substances. The rubbery "state"
of polymers is fairly well understood, but the glassy "state"
is the object of considerable dispute. It has been proposed,
by Gibbs and DiMarzio and others, that T_g is in fact not very
different from a thermodynamic transition temperature, T_2,
which is defined as a temperature that corresponds to the
vanishing of free volume upon cooling. The existence of a
temperature T_2 is postulated as being necessary in order to
avoid the paradox of a lower entropy for amorphous regions
than for crystalline regions with decreasing temperature.
The state of this argument is in considerable doubt. It
would be greatly aided if there were extensive measurements
and correlated models as to the role of pressure-sensitive
parameters such as the heat capacity, the thermal expansion
coefficient, and the molar volume. Data on such parameters
are sparse and often conflicting.

Elevated pressures and major pressure gradients are
common to the important commercial processes of extrusion and
molding of polymers. The absolute pressures are not great,
but since the materials are characterized by quite large
compressibilities in the molten state, gradients in pressure
are empirically found to be important. For example, in the
extrusion of a molten polymer such as polyethylene, there is
found to be a limiting condition of mechanical shear forces

and temperature for a compound of given molecular weight (M.W.)
and M.W. distribution at which a turbulent effect develops.
This phenomenon has sometimes been called "melt fracture",
a term that is outwardly descriptive but not authentic in
molecular terms. With the acute demand for higher efficiency
in the processing of plastics, the contributions of high pres-
sure and of pressure gradients will have to be explored in
vastly greater scope than has been undertaken so far.

APPENDIX L

HIGH-PRESSURE EQUATION OF STATE AND LATTICE DYNAMICS STUDIES

by C. A. Swenson

Iowa State University, Ames, Iowa

Static high-pressure experiments to determine the
thermodynamic properties of solids can use bulk measure-
ments, x-ray and neutron diffraction techniques, or ultra-
sonic velocity measurements.[1] The highest pressure data
have been achieved with x-ray methods,[2] while the greatest
precision (at relatively low pressures) is obtained in elas-
tic constant determinations using ultrasonic methods.[3] The
primary interest in these equation of state (EOS) data
(phase transitions are not included) is fundamental and
involves, for instance, correlations between classes of solids
or tests of theoretical models for a given solid. In this
sense, the maximum information about lattice properties could
be obtained by studies of lattice vibration properties
(lattice dispersion relations) of single crystals as a func-
tion of both temperature and pressure using inelastic neutron
scattering experiments. These experiments are possible
only for the highly compressible rare gas solids for which
significant density changes can be realized at small pres-
sures (a few kbar) in fairly thin-walled aluminum or stainless
steel pressure vessels.[4] The scattering of neutrons from
pressure vessel walls is a major source of background in ex-
periments of this type and provides a practical limitation
to the pressure range hence to the substances which can be

studied. Somewhat the same type of information is obtained
from ultrasonic measurements on single crystals for various
wave polarizations and directions of propagation, although
the data are restricted basically to the low frequency end
of the lattice vibration spectrum. At present, these ex-
periments are being carried out at pressures (of up to 10
kbar) where the second-order effects in the pressure depen-
dence of the elastic constants (proportional to P^2) are im-
portant.[3] The need for hydrostatic pressure to obtain data
for single crystals restricts somewhat the pressure range
which is available. X-ray[1] and neutron diffraction[5] mea-
surements of lattice parameters can be used to obtain infor-
mation about linear compressions of anisotropic solids, with
x-ray data extending at room temperature to 450 kbar.[2]
Single-stage bulk piston displacement measurements of vol-
ume compressions can be made to roughly 40 kbar,[6] although
Bridgman reported compression data to approximately 100 kbar
with a two-stage system.

The usefulness of all of these data in a technolo-
gical sense probably is second-order; they are needed to con-
vert other data from a pressure dependence to a more useful
volume dependence or to provide the more detailed informa-
tion required for a fundamental understanding of another
phenomenon such as superconductivity or the equilibrium be-
tween two crystallographic phases. Guidelines exist[7] so
that available data can be utilized to predict qualitatively
tne high-pressure EOS for a new alloy or compound, although
the need sometimes arises for a direct determination. More
subtle problems can be studied only through direct experi-
ments. For instance, lattice instabilities that are believed

to be associated with superconducting behavior[8] and with the occurrence of some crystallographic transformations[9] can be studied only through the transverse lattice vibrational dispersion relations or, alternatively, the pressure dependence of the elastic shear constants of the solid. In these instances, a study of the EOS (in a general sense) possibly can lead to a more fundamental understanding of the phenomena involved and thus could be of considerable technological importance.

REFERENCES

(The following references are intended to be typical of current approaches in the various areas, and are not to be considered as complete in any sense.)

1. H. G. Drickamer, Comments on Solid State Physics, 1, 11 (1968).

2. H. G. Drickamer, R. W. Lynch, R. L. Anderson, and E. A. Perez-Abbuerne, Solid State Physics, 19, 135 (1966).

3. Z. P. Chang and G. R. Barsch, J. Phys. Chem. Solids, 32, 27 (1971).

4. V. J. Minkiewicz, T. A. Kitchens, F. P. Lipschultz, R. Nathans, and G. Shirane, Phys. Rev., 174, 267 (1968).

5. T. G. Worlton, R. M. Brugger, and R. B. Bennion, J. Phys. Chem. Solids, 29, 435 (1968).

6. S. N. Vaidya and G. C. Kennedy, J. Phys. Chem. Solids, 31, 2329 (1970); ibid., 32, 951 (1971).

7. C. A. Swenson, J. Phys. Chem. Solids, 29, 1337 (1968).

8. L. R. Testardi and T. B. Bateman, Phys. Rev., 154, 402 (1967).

9. W. B. Daniels, J. Phys. Chem. Solids, 28, 350 (1967).

APPENDIX M

ELECTRONIC PHENOMENA AT HIGH PRESSURE

by H. G. Drickamer

University of Illinois, Urbana, Illinois

1. INTRODUCTION

There are several areas of solid-state science in which high pressure has had important impact. These involve (1) studies of cohesive energy and the equation of state, (2) studies of morphology and structure, including phase diagrams and the synthesis and recovery of high-pressure phases, (3) studies of translational and rotational motion, and (4), studies of electronic behavior. After a couple of paragraphs outlining the situation of (1), (2), and (3) above, the bulk of this appendix relates to electronic phenomena.

Measurements of compressibility are perhaps the oldest form of high-pressure solid-state research. In recent decades there have been extensive advances based on a number of developments, including the extension of the static pressure range to several hundred kilobars, the development of high-pressure ultrasonic and x-ray diffraction techniques, the development and refinement of shock measurements, the development of techniques for high-pressure p-v measurements down to temperatures of a few degrees K, and, not the least, improvements in the theories of cohesive energy.

Between 1930 and 1945, P. W. Bridgman demonstrated that the first-order phase transition (the rearrangement of atoms into a new lattice) was a common phenomenon. This was perhaps his central contribution to solid-state science. The

study of high-pressure phase diagrams has flourished, aided
by many of the developments mentioned in the preceding para-
graph, as well as the possibility of doing work at pressures
above 100 kbars at high temperature. It has formed the basis
of a synthetic chemistry involving primarily "quenched in"
high-pressure phases which has been significant both in this
country and abroad, especially in France, Japan, and Sweden
(see appendices D and J). For a long time theory did not
keep pace with experiment in this area. Recently, the im-
portant early work of Löwdin and of Born and Huang has been
supplemented by the important analyses by Phillips and by Van
Vechten. For certain relatively simple classes of systems
there appears to be a reasonable possibility of predicting
first-order transitions. The measuring of phase diagrams
of specific materials with potential practical interest, as
well as a certain amount of systematic investigation, will
always be of importance. There are, however, phenomena
associated with first-order phase transitions that are very
imperfectly studied, either experimentally or theoretically.
These phenomena include metastability, which forms the basis
for the quenching in of high-pressure phases, and the rates
of first-order phase transitions including melting. In these
areas experiments are in a rudimentary stage, and adequate
theory is almost nonexistent. These studies would be intense-
ly practical as well as interesting to the scientific com-
munity. Most high-pressure synthesis depends on the possibility
of quenching in a metastable phase. The use of solids as
"cushions" to absorb rapidly high energy pulses depends on
the utilization of the volume change and latent heat associated
with a phase transition and on the rate at which these can be
made available.

In contrast to the situations associated with crystal-
line materials, as described above, the use of pressure to
investigate the morphology of polymers and glasses is in a
much more rudimentary stage. It would appear, however, to
be a field of considerable promise (see appendix K).

A third area of active high-pressure research is
that of atomic or ionic motion in solids. There have been
extensive studies of diffusion in metals in the hydrostatic
range, pioneered by D. Lazarus, as well as some measurements
on ionic and covalent crystals. These studies have been es-
sential to the understanding of the role of impurities in
determining the properties of solids. Decker has recently
extended diffusion measurements into the higher quasi-
hydrostatic range. In addition to the studies of translational
motion usually accomplished by tracer techniques, the use of
nuclear magnetic resonance relaxation methods to follow rotation-
al, translational, and other motions in solids, liquids, and
solutions is a technique of growing significance in chemistry.
In particular, the study of motion in polymers under pressure
has important practical implications.

Somewhat in contrast to the areas discussed above,
the study of the electronic structure and electronic behavior
of solids is strictly a phenomenon of the past 25 years. In
the late 1940's, A. W. Lawson demonstrated that hydrostatic
pressure studies in the 12-kbar range could yield important
information about electrons in solids. This approach has
been pursued vigorously by physicists and most of the measure-
ments of solid-state physics are now made in this pressure
range. The possibility of measurements at a few degrees K

and several kilobars has greatly extended the applicability
of high pressure to the problems of physics.

During the past 15 years it has been demonstrated
that quasi-hydrostatic measurements at higher pressures (in
some cases as high as 500 kbar) are significant to the under-
standing of electronic behavior. The major development has
been the possibility of making a variety of types of measure-
ments that are sensitive to the relative displacement of elec-
tronic and nuclear energy levels at these high pressures.
These include optical absorption and emission (fluorescence
and phosphorescence), nuclear magnetic resonance, Mössbauer
resonance and susceptibility, and dielectric measurements,
in addition to electrical resistance. The extension of the
pressure range has been essential to the discovery of many
of the electronic transitions discussed below. Recently
McWhan and Lyons have developed a technique for making
electrical resistance measurements to 100 kbar at a few degrees
K, which has already had important consequences for the under-
standing of insulator-metal transitions. Jayaraman's extension
of the static pressure range to 50 kbar has been significant
in understanding semiconductor behavior. In this appendix
it will be possible only to outline briefly the basic effect
of pressure on electronic behavior and the types of studies
made, with a few comments about applications.

The essential effect of pressure is to increase
overlap of adjacent electronic orbitals. One result of this
increased overlap is a broadening of energy bands and an in-
creased electron delocalization. A second result is a shift
in the energy of one type of orbital with respect to another.

Since orbitals of different quantum number may differ in radial extent or shape, this is a common phenomenon. Must of our understanding of electronic properties of solids comes from a study of these shifts. For many systems the shifts due to pressure are quite analogous to the shifts in going from a dilute gas to a solution, but the pressure shifts are frequently more susceptible to analysis.

Many systems have excited states which lie not too high in energy with respect to the ground state. For such systems the relative shift in energy may be sufficient to give a new ground state for the system, or a ground state grossly altered by configuration interaction. This event is called an electronic transition. These events may occur discontinuously at a fixed pressure or over a range of pressures. The prediction, discovery, and elucidation of electronic transitions is one of the most important aspects of solid-state science. It has primarily been an activity associated with physics, but it has recently been demonstrated that electronic transitions can also have significant chemical consequences.

The above phenomena can be described in terms of one electron theory. Pressure also has significant effects in truly cooperative phenomena such as ferromagnetism and anti-ferromagnetism, ferro-electricity, and superconductivity. In such a brief discussion, however, it is possible only to touch on those areas where high-pressure studies have had important impact and to include a few predictions about future possibilities.

The measurement of the shift of energy levels with pressure has been important to a wide variety of problems, both

theoretical and applied. The shifts of the absorption edge
in semiconductors, and the evaluation of the deformation
potential is an important feature in the design of electronic
components. Shifts of the absorption edge also play a role
in the study of the approach to the metallic state discussed
below. High-pressure studies have been important in under-
standing the nature of color centers in alkali halides and
of other impurity centers in a variety of crystals. High-
pressure studies of transition metal ion spectra in a wide
variety of environments is a very significant feature of co-
ordination chemistry, High-pressure optical studies have
similarly contributed to our understanding of the π energy
levels of aromatic compounds. Both absorption and emission
measurements (fluorescence and phosphorescence) and been
important in this regard. Finally, high-pressure optical
studies have made a basic contribution to the analysis of
forces involved in electron donor-acceptor complexes.

2. ELECTRONIC TRANSITIONS

One of the most active branches of high-pressure
experimentation is the prediction, discovery, and explanation
of electronic transitions — new electronic ground states. As
we shall indicate below, these new ground states may have
different chemical as well as physical properties. They may
also have geophysical and biological implications.

Table 1 may be helpful in trying to understand the
nature of these transitions. The types of transitions observed
in solids are divided into four classes. Class I refers
to events that involve rearrangement of the atoms, ions, or
molecules with no electronic implications. Class II contains

TABLE 1 - <u>Types of High-Pressure Transformations</u>

Class I 1st Order Transition- Electronic Negligible	Class II 1st Order Transition- Significant Electronic Component	Class III Electronic Transition- Significant Volume or Structure Change	Class IV Electronic Transition- Continuous
fcc → sc KCl,KBr,KI	bcc → hcp Iron (Ferro → paramagnetic)	s → d Cesium Rubidium Potassium?	reduction of Fe(III) to Fe(II)
fcc → hcp Lead	diamond → white tin Si,Ge,InSb,GaAs etc. (semiconductor → metal)	f → d cerium other rare earths	spin changes in partially filled shells
		Mott Transition doped V_2O_3?	reactive ground states of aromatic hydrocarbons and electron donor-acceptor complexes
			rare earth salts

events whose main feature appears to be polymorphism, but where there may be drastic changes in electrical or magnetic properties. Class III contains essentially electronic transitions that occur discontinuously and are accompanied by a volume discontinuity. Class IV involves new ground states established over a range of pressures, cooperative phenomena, or events involving continuous change in the degree of configuration interaction. The equilibrium between states here is like the equilibrium between reactants and products in any chemical reaction.

The boundaries between the various classes are, of course, somewhat arbitrary. Any rearrangement of atoms or ions implies some change in electronic interaction because of change of local symmetry. Whether the electronic component of a transition is major or minor is, to some degree, a matter of viewpoint. Whether a transition occurs continuously or discontinuously may depend on the temperature at which it is studied. Nevertheless, the classification affords a basis for understanding many electronic phenomena. Outlined below are three classifications of electronic transitions -- those in metals, insulator-metal transitions, and those in organic and inorganic insulators.

a. Metals

Electronic transitions were first discovered in metals. Over 20 years ago a cusp in the resistance of cesium near 40 kbar was associated with a change in character of the conduction band from 6s to 5d. A second transition was discovered some ten years ago which is probably associated with the introduction of 4f and 5d characters to the conduction band. A sharp rise in the resistance of rubidium near 145 kbar probably involves

involves a 5s → 4d promotion, and a maximum at 300 kbar may
be established by introduction of 4p character. Potassium
exhibits a sharp resistance rise near 280 kbar at low tem-
perature probably associated with a 4s → transition. The
magnitude decreases with increasing temperature and it dis-
appears near 250° K. This may be an example of a critical
point for an electronic transition.

Some rare earth metals also exhibit electronic tran-
sitions probably involving promotion of a 4f electron to the
5d shell or to the conduction band. The transition in cerium
has been most thoroughly studied as it initiates at a few kbar
pressure. It has been shown that it disappears at a critical
point with increasing temperature. There are numerous cusps
and resistance maxima in various rare earth metals (e.g.,
praesidymium, neodymium, europium, etc.). In several cases
these are very sharp at low temperature and broaden out near
room temperature so that there may be critical points for
these transitions. In addition to these static high-pressure
studies to pressures of 500 kbar, there have been shock-wave
studies to well over a megabar. These reveal discontinuities
in compressibility at very high pressure and temperatures of
several thousand degrees Kelvin. It is, of course, difficult
to interpret events electronically when the thermal energy
is a significant fraction of an electron volt.

Finally, metals like calcium, strontium, and ytter-
bium exhibit a metal to semiconductor or metal-semimetal tran-
sition. The free atoms of these materials have filled
electronic shells, and they are metals because the conduction
band is of s-p-d character. The Fermi surface has thus a
complex intersection with the Brillioun zone boundary. With

pressure the holes and overlaps merge to give semiconducting
character. At sufficiently high pressure, there is a first-
order phase transition to a metallic state.

b.   Insulator-Metal Transitions

In a simple band picture of solids, insulators have
filled bands separated by energy gaps large compared with kT.
Metals have partially filled bands or filled bands overlapping
empty bands as in the alkaline earth metals discussed above.
Since many transition metal oxides are insulators, although
in the simple picture the partially filled band arising from
the atomic d orbitals should give metallic conductivity, it
is clear that more than the simple picture is needed. Mott
has developed an analysis that predicts that such materials
will be insulators below a certain electron density and metals
above that density.

Since increasing pressure tends to broaden energy
bands and to shift one set of bands with respect to another,
one might expect that insulator-metal transitions would occur
by a number of different mechanisms with increasing pressure.
In molecular crystals like iodine or pentacene, metallic
conductivity occurs at sufficiently high pressure with no
apparent discontinuity in physical properties. It would appear
that in these very compressible materials the primary mechanism
is the broadening and shift of energy bands.

Silicon, germanium, and the related III-V compounds,
which are useful transistor materials, exhibit the diamond
(zinc blende) structure which is relatively open. At sufficient-
ly high pressure these materials show first-order transitions
to the white tin or an analogous structure which is metallic.

Van Vechtin has developed a theory which is remarkably success-
ful in predicting the pressure associated with these transitions.
This theory should be useful in predicting the possibilities of
transitions of a practical nature.

Compounds like ZnS, ZnSe, ZnTe, and CdS also have
the zinc blende (or wurtzite) structure. Since these are
practical phosphors, the understanding of their properties is
of practical importance. The zinc compounds transform at
high pressure to a form of low resistivity and metallic or
semimetallic behavior. They apparently have the NaCl structure.
The high-pressure phase of ZnS exhibits a maximum in resistance
near 425 kbar with a drop of about 25% by 500 kbar. CdS
transforms to the NaCl structure at 25 kbar. The high-pressure
phase is semiconducting and exhibits a large maximum in
resistance near 330 kbar with a drop of 40% by 450 or 460 kbar.
The unusual resistance behavior in the NaCl phases of ZnS
and CdS may involve further electronic transitions. A thor-
ough study could reveal information of importance about these
useful materials.

The transition metal oxides have been widely studied.
Perhaps the most broadly bases, thorough, and useful study has
been by McWhan and his colleagues at Bell Laboratories. Their
studies on mixed V_2O_3-Cr_2O_3 crystals have been especially
interesting. The material $V_{0.96}Cr_{0.04}O_3$ can exist as either
a paramagnetic or antiferromagnetic insulator or a metal
depending on the pressure and temperature. The insulator-
metal transition approximates very closely to the transition
predicted by Mott. An important feature of the McWhan study
is the relationship exhibited between changing chemical com-
position and changing pressure on electronic properties.

There are many ways in which changing pressure has effects
analogous to changing composition in a wide variety of solids
and liquid solutions. For many systems pressure can be used
as a simple way of explaining and predicting composition
effects. This has not been hitherto widely understood. This
understanding could lead to the "design" of solids which, at
one atmosphere, would have the desirable properties which may
first be observed only in materials under very high pressure.

Insulator-metal transitions have also been observed
in rare earth calcogenides. These are associated with changes
in the occupation of the 4f orbitals and may occur discontin-
uously or over a range of pressure.

c. Insulators

Electronic transitions have been observed in a
variety of insulators with consequences of considerable chem-
ical importance. The relative shift of electronic orbitals
with pressure, combined with increased configuration inter-
action can give a new ground state with very different chemical
properties. These transitions typically fall in Class IV of
Table 1.

Aromatic hydrocarbons with low-lying excited states,
such as pentacene and hexacene, react at high pressure and
room temperature to form highly stable polymers. The reaction
takes place via thermal occupation of the polar, reactive,
excited state at high pressure. Some hydrocarbons, like
pyrene and perylene, have excited states too high in energy
to be thermally accessible at the highest available pressures,
so they are not reactive. They form donor-acceptor complexes
with acceptors such as iodine. These complexes have low

lying excited states that can be thermally occupied at high pressure. These materials then react. The iodine can be recovered qualitatively from the product leaving dimers and tetramers of the hydrocarbons of a type not hitherto seen. It is thus possible, by means of an electronic transition, to create a new class of hydrocarbon compounds.

A combination of Mössbauer resonance and optical absorption has revealed an extensive high-pressure chemistry of iron compounds. There are at least three kinds of electronic transitions resulting from interaction of the ligands (the surrounding atoms or ions) with the iron. The normal state of iron in ionic compounds is high spin. Transformations to the diamagnetic low-spin state have been observed, resulting from the increase in the splitting of the iron 3d orbitals by the field of the ligands at high pressure. Low-spin compounds exist if the ligands have available orbitals of appropriate energy and symmetry (π^* orbitals) which can be occupied by metal d_π electrons. This "back donation" provides the large ligand field necessary to give a low-spin ground state. At sufficiently high pressure the ligand excited states are occupied by ligand π electrons by a process similar to that observed for the aromatic hydrocarbons discussed above. This forces the metal electrons back into the metallic 3d orbitals and results in a low-spin to high-spin (diamagnetic-paramagnetic) transition. This can be classified as an "induced electronic transition," since a transition on the ligand induces one on the iron.

Finally, the reduction of ferric iron to the ferrous state is frequently observed. This takes place because the

3d orbitals lower in energy, vis-a-vis the ligand nonbonding
orbitals, until the electron transfer is feasible. All of
these processes take place over a range of pressures and are
reversible, with considerable hysteresis. An analysis has
been presented which accounts for the continuous nature of
the process and for the hysteresis.

All the processes described here are thermal processes
resulting from the relative shift of one type of orbitals with
respect to another. Such shifts are normally measured by optical
absorption. There are a number of reasons why optical processes
involve different energies from thermal processes. These include
the Franck-Condon principle (optical processes are rapid com-
pared with nuclear motions), differences in selection rules,
differences in the configuration coordinates involved in the
two types of processes, and the effect of configuration inter-
action. An analysis has been presented which relates the two
processes and which permits the prediction of thermal electron
transfer from optical absorption studies. Specifically, the
thermal energy is given approximately by the relationship

$$E_{th} \cong h\nu_{max} - \frac{1}{16\ln 2} \frac{(\delta E_{\frac{1}{2}})^2}{kt} \left(\frac{\omega'}{\omega}\right)^2$$

where ν_{max} is the frequency of the maximum in optical absorp-
tion, $\delta E_{\frac{1}{2}}$ is the full width at half maximum for the optical
peak, and ω and ω' are force constants associated with the
ground and excited states. This relationship permits a semi-
quantitative prediction of the pressure at which a (thermal)
electronic transition will occur, from high pressure optical
absorption data.

3. COOPERATIVE PHENOMENA

As mentioned earlier, there are classes of phenomena
which can only be described in terms of interactions of elec-
tronic arrays. These include ferromagnetism, antiferro-
magnetism, ferroelectricity and superconductivity. Samara
discusses ferroelectricity in Appendix I. In ferromagnetism
and antiferromagnetism the relevant measurements are for
the effect of pressure on the size of the field and on the
Curie (or Néel) temperature. These studies have been impor-
tant in understanding electron-electron correlations, alloy-
ing effects, "giant moments" in palladium alloys, and spin
states in metals, as well as super-exchange and related phe-
nomena in insulating antiferromagnets.

Pressure has been important in superconductivity
research. Changes in critical temperature with pressure
have formed important tests of theories. Most spectacular
has been the creation of new superconducting phases at high
pressure, and especially the superconductivity of metastable
phases. The possibilities of high-temperature superconduc-
tors, especially hydrogen, have been widely discussed (see
Appendix G).

4. PROSPECTS AND APPLICATIONS

Much of the work on electronic behavior at high
pressure involves processes of current practical importance.
In a number of cases (e.g., semiconductors) the work has
been rather directly relevant to engineering design. Studies
of pressure and electronic structure will continue to be a
significant part of basic research. Listed below are several

aspects where such studies would appear to be rather directly
relevant in the near future:

a. The study of high temperature superconductivity.

b. An elucidation of the properties of ferrites as
related to local symmetry and orbital overlap.

c. A better understanding of luminescence.

d. New chemical reactions and new products based on
novel electronic ground states. In this connection
an important aspect is the ability to predict elec-
tronic transitions from optical absorption data.

e. An understanding of the relationship between pres-
sure effects and effects of changing composition
to permit one to obtain at one atmosphere materials
with properties only presently accessible at high
pressure or in high-pressure phases.

f. An understanding of the mechanism of protein
denaturation.

In the past two decades high-pressure studies of
electronic behavior have been very largely the domain of the
solid-state physicist. There will be a considerable rela-
tive increase in the fraction of this activity relevant to
chemical (and biochemical) problems.

Reviews devoted in large part to electronic phe-
nomena include:

W. Paul and D. Warschauer, (eds.),"Solids Under
Pressure," McGraw-Hill, New York 1963.

C. T. Tomizuka and R. Emrick, (eds.),"Physics
of Solids at High Pressure," Academic Press,
New York 1965.

D. Bloch, (ed.) "Proprietes Physiques des Solides
Sous Pression," CNRS, Paris 1969.

D. B. McWhan, "The Pressure Variable in Materials
Research," Science 176, 751 (1972).

H. G. Drickamer and C. W. Frank, "Electronic
Transitions and the High Pressure Chemistry
and Physics of Solids," Chapman and Hall, London,
February 1973.

There are also articles in "Solid State Physics," F. Seitz,
D. Turnbull and H. Ehrenreich (eds.), especially Vols. 11,
13, 17 and 19, Academic Press, New York, and in various
volumes of "Advances in High Pressure Research," R. S.
Bradley (ed.) and R. H. Wentorf (ed.), Academic Press,
New York.